Forms and mechanisms for phosphorus leaching in an alluvial soil.

A dissertation submitted in
partial fulfilment of the requirements
for the Degree of

Master of Water Resource Management
at Lincoln University.

By Wayne Richard Worth.

Lincoln University

2017.

Forms and Mechanisms for Phosphorus leaching in an alluvial soil.

By

W.R.Worth.

Abstract.

The fresh water quality of New Zealand is considered very clean by international standards however in dense urban and rural areas the water quality has degraded. Economic incentives of a high milk solid price has led to an increase in dairy herds and milking platforms in many regions. The conversion of lowland dry stock pastures into dairy units has been widespread in some of the most vulnerable regions prone to leaching. Many of these areas contain glacial outwash fans and till deposits of gravels and sands covered by thin soil layers, which are characterised as having low Anion storage capacity (ASC) and a high potential to leach phosphorus (P) under irrigation.

Leaching studies utilising monolithic soil lysimeters and lab based leaching experiments were undertaken on soils taken from a recently established dairy unit, that occupies part of the Manuherikia River flood plain within the Alexandra basin of Otago, New Zealand. The research objective was to study the potential for P to move down the vadose zone and into groundwater from common P applications under irrigated and grazed dairy pastures.

This was addressed by firstly examining the bioavailability of different organic P forms leached in these gravels, secondly, to determine if low ASC gravel soils coincide with enhanced vertical P loss and thirdly, estimating how long intensive farming of these areas would take to enrich groundwater P.

Results indicate that although there is attenuation of P occurring within the root zone, the low ASC of the soil leads to significant loss of P towards the vadose zone. A median value of 0.273 mg/l filterable reactive P (FRP) at 1m depth was determined in the receiving gravels of the study area, which exceeds the ANZECC 2000 guidelines trigger value of 0.010 mg/l FRP for lowland rivers. There is also evidence that the majority of loss occurs in the form of preferential flow.

This is also enhanced by dung, due to the inhibition of P sorption sites by organic compounds in dung and increases the incidence of labile organic forms of P moving downward towards ground water. There is a strong argument that current concentrations of P potentially reaching ground water underlying these soils, pose a risk to surface water quality.

Keywords

Phosphorus, low P retention, Anion storage capacity, liable organic P, irrigation, vadose zone, ground water, dairy.

Contents.

Figures and Tables.

Chapter One: Introduction.

Phosphorus (P) is one of the main nutrients generally added to soils in the form of fertilizers, one of the main roles of P in living organisms is in the transfer of energy. Organic compounds that contain P are used to transfer energy from one reaction to drive another reaction within cells.

Phosphorus is an essential element classified as a macronutrient because of the relatively large amounts of P required by plants. Adequate P availability for plants stimulates early plant growth and hastens maturity. Although P is essential for plant growth, mismanagement of soil P can pose a threat to water quality. The concentration of P is usually sufficiently low in fresh water so that algae growth is limited, however when lakes and rivers are enriched with P, excessive growth of algae often results.

Phosphorus is found in nature in various forms: mineral forms, organic forms (such as phospholipids, nucleic acids and proteins), gaseous forms, particulate or colloidal forms and dissolved inorganic forms" (Valls-Cantenys et al. 2012).

Research conducted within New Zealand has highlighted conditions where P loss to groundwater, is thought to be enhanced. These are: high soil Olsen P concentrations, soils with low anion storage (i.e. poor P sorption), and irrigation, which may regularly induce leaching to the vadose zone.

There has been abundant studies conducted on subsurface and groundwater transport of P in recent years. This review will examine the published literature regarding P loss to groundwater, transport to surface waters and its relationship with the management of soils vulnerable to P loss.

1.1. Phosphorus cycle.

Phosphorus (P) is a primary plant nutrient. Unlike nitrogen, P is not part of the atmosphere. Instead, it is found in rocks, minerals, and organic matter in the soil. The mineral forms of P are apatite, which may be in a carbonate, hydroxide, fluoride, or chloride form, and iron or aluminum phosphates. These minerals are usually associated with basalt and shale rocks. Chemical reactions and microbial activity affect the availability of P for plant uptake. Under acid conditions, P is held tightly by aluminum and iron in soil minerals. Under alkaline conditions, P is held tightly by soil calcium.

Although P is widely distributed in nature, P is not found by itself in elemental form. Elemental P is extremely reactive and will combine with oxygen when exposed to the air. In natural systems like soil and water, P will exist as phosphate, a chemical form in which each P atom is surrounded by 4 oxygen (O) atoms. Orthophosphate, the simplest phosphate, has the chemical formula PO_4^{-3}.

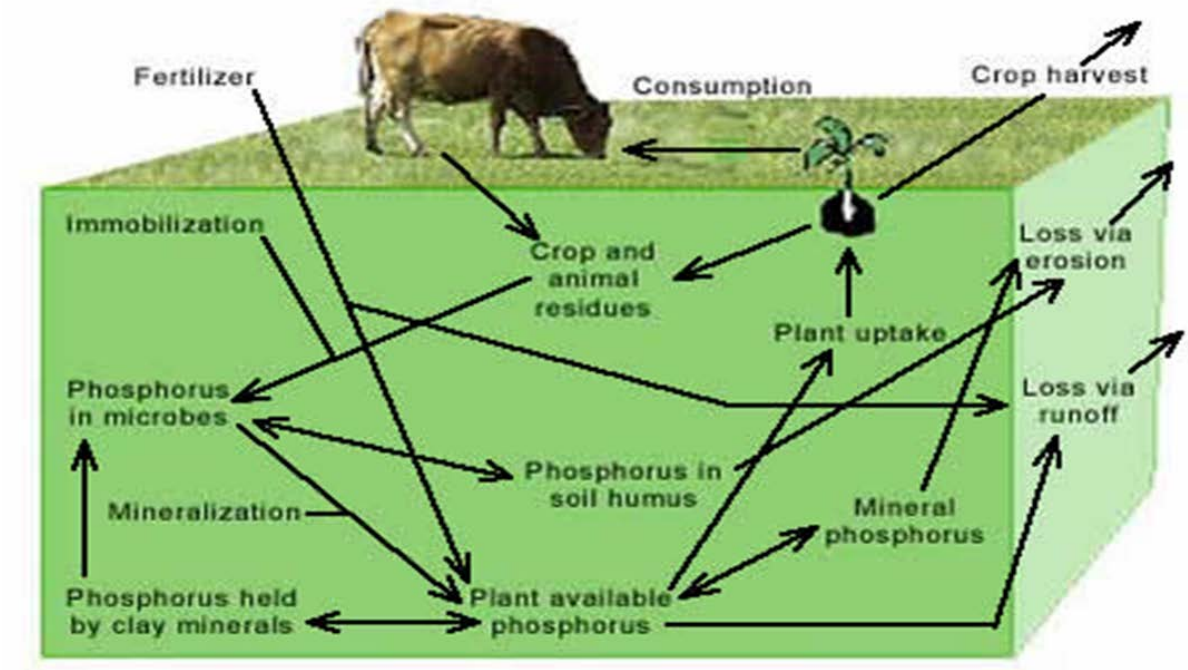


Figure 1: Phosphorus Cycle.

The P cycle (Fig.1) is affected by microbial and chemical transformations. Soil organisms mineralize or release P from organic matter. Soil-bound P can be lost due to erosion while runoff waters can transport soluble P found at the soil surface.

Plants use P for energy transfer and reproduction. Legumes require P for effective nitrogen fixation. Animals consume P when they eat forages. Phosphorus not used for animal growth is returned to the soil in manure. Following decomposition by soil organisms, P again becomes available for plant uptake (Figure 1).

Much of the phosphate used by living organisms becomes incorporated into organic compounds. When plant materials are returned to the soil, this organic phosphate will slowly be released as inorganic phosphate or be incorporated into more stable organic materials and become part of the soil organic matter. The release of inorganic phosphate from organic phosphates is called mineralization and is caused by microorganisms breaking down organic compounds. The activity of microorganisms is highly influenced by soil temperature and soil moisture (Busman et al. 2009). The main sources of potentially mobile P are fertilizers, manure, plant residue and P contained within soil.

1.2. Use of phosphate rock in fertiliser.

"The *Green Revolution* was a period in the mid-20th century (1930-1960) when the productivity of global agriculture increased drastically as a result of new advances and technology transfer. During this time period, new chemical fertilisers have made it possible to supply crops with extra nutrients and, therefore, increase yields. Synthetic herbicides and pesticides were also created contributing to increase yields. The production of P mineral fertilisers uses phosphate rock (PR), a rock rich in the mineral fluorapatite [$Ca_5 (PO_4)_3F$] and phosphoric acid [H_3PO_4], which comes mainly from the treatment of PR with concentrated sulphuric acid. Single superphosphate was the first commercial P mineral fertiliser and is manufactured from the reaction between sulphuric acid and PR. Whereas triple superphosphate (TSP) fertiliser is produced by the action of concentrated phosphoric acid on ground phosphate rock. Also, ammoniated phosphates (mono-ammonium phosphate- MAP and di-ammonium phosphate- DAP) are manufactured with phosphoric acid (Horta 2015).

By far the largest use of phosphoric acid is in the manufacture of phosphates for use as fertilizers (Figure 2).

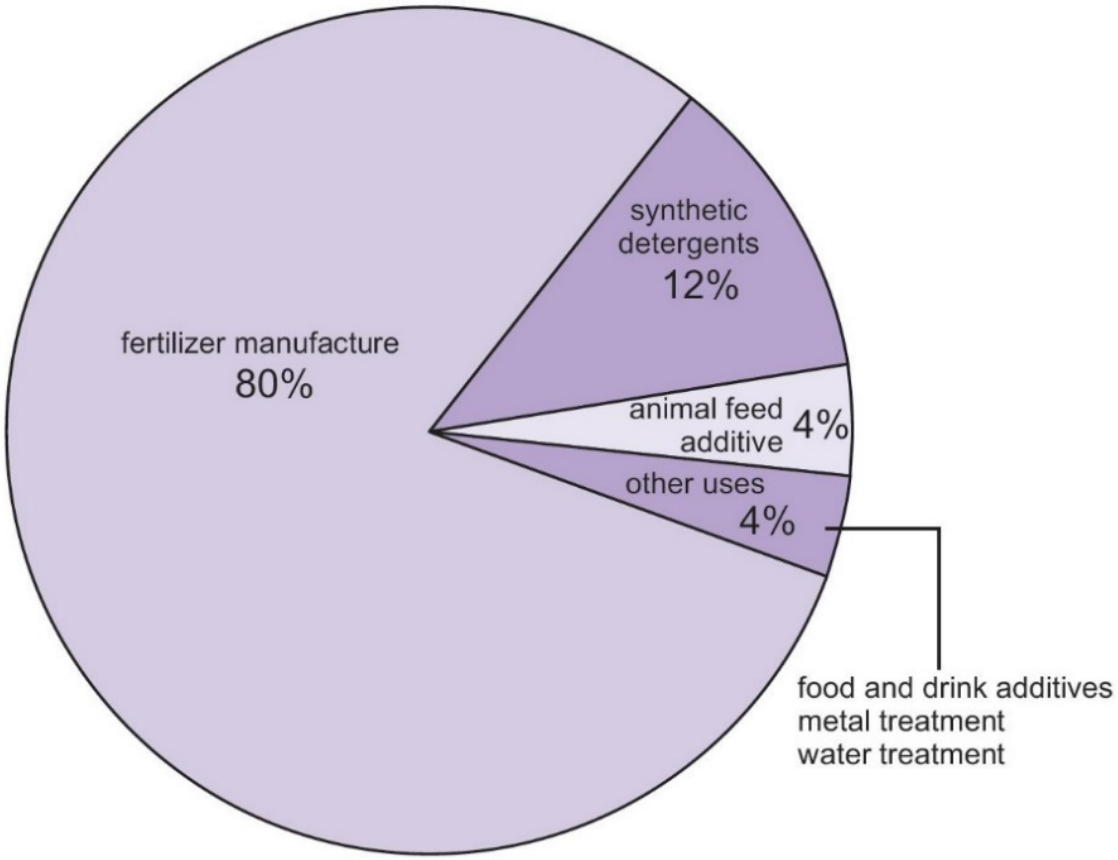


Figure 2: Uses of phosphoric acid.

http://www.essentialchemicalindustry.org/chemicals/phosphoric-acid.html.

Most of the world's soils are P deficient and the building of P reserves is a long established soil fertility practice, as is the maintenance of soil P at levels sufficient for crop growth. However, P applied in excess of crop requirements and the capacity of the soil to retain the P is not well addressed in most agronomic practices, leading to an abundance of manure P. (Kleinman et al. 2011).

1.3. Phosphate sustainability.

The economic importance of phosphate and its conservation has been broached in the past, in 1938, US President Franklin Roosevelt said it was “High time for the nation to adopt a national policy for the production and conservation of phosphates for the benefit of this and coming generations”. However a comprehensive policy was not adopted (Elser et al 2011). Phosphate rock is a finite natural resource and cannot be extracted forever to compensate for its use. Global food production relies on the provision of economically available supplies of inorganic fertilisers.

As noted by Childers (2011), there is no known chemical or technological substitute for P in either natural ecosystems or in the agrosystems that produce food and commodities, this coupled with the fact that the natural P cycle operates in geological time scales means that the increasing demand for this resource will lead to higher prices for dwindling economic supplies. As with oil, P resources are expected to “Peak” around about 2030 (Cordell et al. 2009), and are increasingly moving towards being a strategic mineral for many counties, who want to secure supply for their domestic production (Elser et al. 2011).

Most PR used in fertiliser production is sedimentary (>80%), but igneous deposits are also used and were formed mostly in shield areas and rift zones (Figure 3).

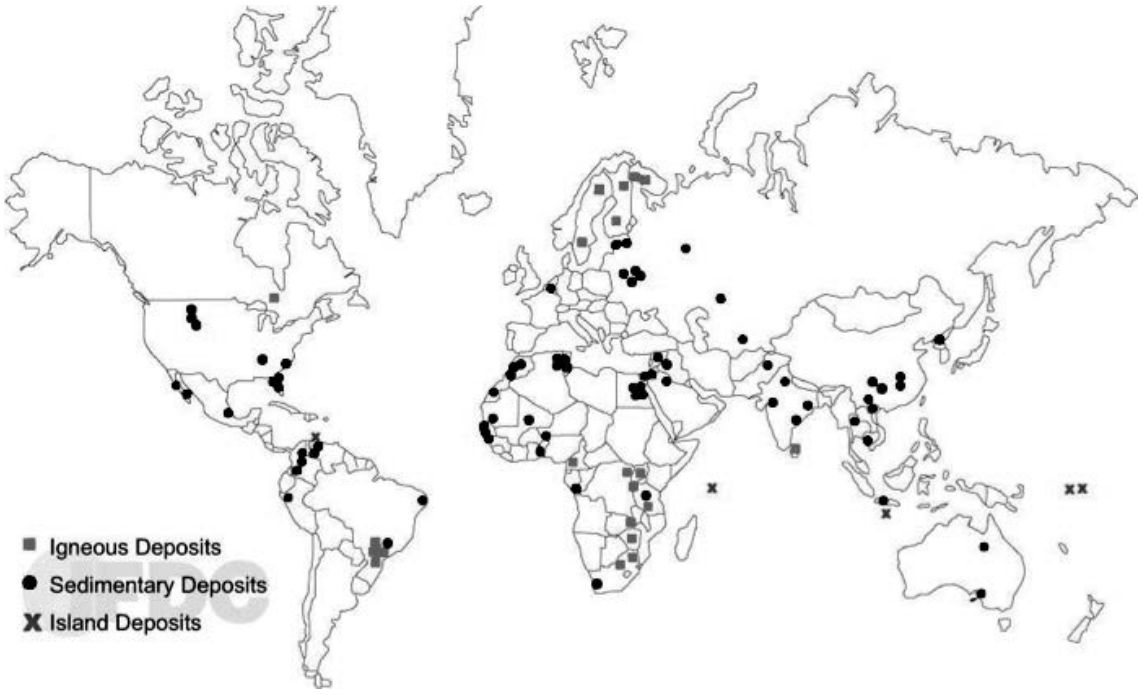


Figure 3: Location of world phosphorus resources Source: Zapata (2004).

1.4. Eutrophication of fresh water surfaces and coastal oceans.

The anthropogenic eutrophication of aquatic ecosystems due to diffuse pollution of agricultural P is a water quality problem that can be found globally. Anthropogenic inputs of P have dramatically increased over the last century and in the first world and increasingly in the developing world, nutrient transference by farming systems has overwhelmed natural cycles and led to P accumulation in agricultural soils. And as the P content in soil increases, so to the amount of P lost to surface water rises (Carpenter et al. 1998).

The management of agricultural sources of P and the potential for eutrophication is however difficult, as the task is hindered by the complexity of catchment processes, variability of management practices and variation in climate conditions. The balance between what is economically viable to the farm system is being balanced against what is required to keep receiving waters below a tropic state of decline (Kleinman et al. 2011).

1.5. Bioavailability to aquatic processes.

Bioavailable P is defined as the sum of immediately available P and the P that can be transformed into an available form by naturally occurring processes. It is important to distinguish between different forms of P because of their different adsorption-desorption reactions, transport and potential bioavailability to aquatic organisms. Bioavailability (what is immediately available for growth) of P describes the different potential of P from various sources of supporting eutrophication (Correll 1998).

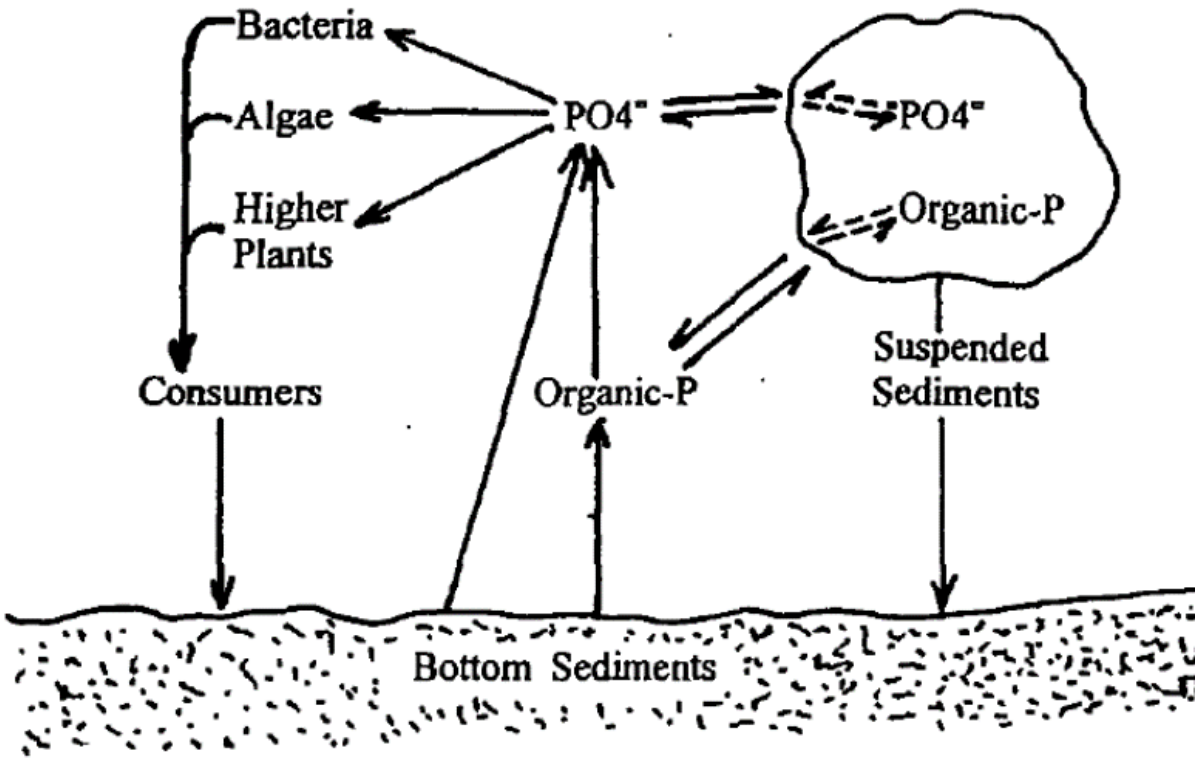


Figure 4: Phosphorus availability in water, (Correll 1998).

Bioavailable P will move between storage sites, re-mobilize in the water column and be available for uptake by consumers (Figure 4).

Commonly used terms to describe P in the forms that effect surface water quality are Filterable reactive P (FRP), which is primarily dissolved orthophosphate (PO_4^{3-}). FRP, usually considered to be that fraction that passes through a 0.45 µm filter (McDowell et al. 2004) is generally considered to be the most labile P form that contributes to eutrophication of surface waters.

The difficulties associated with eutrophication include a decline in drinking water quality, fisheries and water volume or flow. The main causes of these problems being algal blooms, macrophyte and littoral algal growth, altered thermal conditions, turbidity and low dissolved solids. Health conditions for human populations can include a range of skin irritations to schistosomiasis (acute and chronic disease caused by parasitic worms) and diarrhoea to potentially toxic cyanobacteria (Winder 2012). While representing a degradation of ecosystem services and a health issue for users of the resource, there is also a large financial cost to the results of eutrophication.

Dodds et al (2009) explored the costs of eutrophication to the United States of America economy and found that when calculations of the potential annual value losses in recreational water usage, waterfront real estate, spending on recovery of threatened and endangered species, and drinking water were totalled, the combined costs were approximately $2.2 billion annually. The greatest economic losses were attributed to lakefront property values ($0.3-2.8 billion per year, although this number was poorly constrained) and recreational use ($0.37-1.16 billion per year). Diffuse loss of P to surface waterways is seen as a major worldwide cause of eutrophication in rivers, lakes, estuaries and coastal oceans (Carpenter et al. 1998).

New Zealand has an abundant supply of freshwater, on an average annual basis. However, water demand has grown in many areas due to agricultural development. Intensive dairy farming and dairy support has been identified as being a cause of nutrient enrichment of waterways (Hamill et al. 2003). The fresh water quality of New Zealand is considered very clean by international standards, however in dense urban and rural areas the water quality has degraded. Subsequently, a balancing act is required by government to help preserve local water bodies as a high quality resource, while enabling primary industry to continue with increased productivity to benefit the economy.

Increasingly, reviews of P losses from agricultural point toward diffuse or non-point pollution from intense production systems as being a less understood contributor to anthropogenic eutrophication in the past (Holman et al. 2008; Kleinman et al. 2011). The control of non-point diffuse sources of P is an important knowledge gap and a future research direction (Krovang et al. 2009, Delgado et al. 2008, McDowell et al. 2012).

Of particular interest to some New Zealand researchers is the effects of large scale development of alluvial soils into intensive dairy units with a high potential to leach nutrients under grazed pasture (Carrick et al. 2014; McDowell et al. 2013; Gray 2015).

1.6. Forms and sources of phosphorus.

Phosphorus plays a vital role in determining the function of productivity in terrestrial and aquatic systems. Phosphorus dynamics in natural and managed ecosystems are determined to a significant extent, by the complex nature of the interactions between the different forms of inorganic, organic and microbial P (Condron et al. 2011). In New Zealand agriculture the use of P fertilizer, the inputs of animal dung deposited direct to paddock and the use of farm dairy effluent (FDE) has contributed greatly to increased amount of P contained within the ecosystem. Therefore, it is practical to accept that as concentrations of P increase, so does the potential for mobility and transformation.

1.6.1. Organic P.

Organic forms of P include labile (combination of mineral and organic P) phospholipids, nucleic acids, inositol's, fulvic acids and humic acids. This labile form of P undergoes reactions that see the simultaneous transformation of organic P to inorganic P (mineralisation) and the reverse where inorganic P is converted to organic P (immobilisation) (McDowell et al. 2001; McLaughlin et al. 2011). The cycling of organic P through available microbial biomass pools is also an important indicator of soil P availability, (Khan et al. 2012). Khan et al (2009) in a trial evaluating microbial biomass P in amended compost, observed that the stimulation of microbial biomass and incorporation of P into microbial cells occurred immediately after inorganic P addition, as microbial biomass rapidly stored easily soluble P preventing adsorption or other fixation processes.

1.6.2. Inorganic P.

In the soil profile, P exists in both inorganic and organic forms. Inorganic P has over 150 different mineral forms and varies in its solubility and ability to supply the soil solution with P. Factors that influence the solubility have been shown to include soil type, pH, the concentration of aluminium (Al), iron (Fe), calcium (Ca) and magnesium (Mg) and the concentration of anions that compete with P for exchange sites (Ligand reaction). P minerals generally have a low solubility and as such, the concentrations in the soil solution are low. The most abundant accepted form of soluble P available for plant uptake being orthophosphate, which is highly bioavailable to algae.

1.6.3. Excreta as a source of P.

In grazing systems worldwide, excreta (dung) has been used as an important source of nutrients to increase soil fertility and lift pasture production. As the scale of the farming system increases from small farm lots running modest sized herds, to large intensive operations that rely on commercial nutrient options such as fertiliser for production, accounting for manure inputs becomes problematic.

Losses of P from grazed pastures have been shown to come from fertilizer, soil, dung, and unused forage (McDowell et al. 2007). The effects of long term exposure of pasture to animal excreta is a concern for many researchers as it has been shown to increase overall P levels in soils with time (Carpenter et al. 1998; McDowell et al. 2004; Kleinman et al. 2011) amongst others, and has implications for the management of nutrient cycling within catchments (McDowell et al. 2011).

A review conducted by Edmeades (2003) compared the results of 14 long term (20 to 120 year) field trials to quantify the effects of manures and fertilisers on soil productivity. The results showed that manured soil had a higher content of organic matter and numbers of micro fauna than fertilised soils. Manured soils also had a lower bulk density and higher porosity, hydraulic conductivity and aggregate stability, relative to fertilised soils and excessive accumulation of some nutrients, particularly P and N from the long-term use of manures, relative to fertilisers.

The increase in New Zealand of instances where dryland pastures are exposed to irrigation through conversion to dairy blocks can, escalate nutrient enrichment. McDowell et al (2015) in a meta-analysis of published data found evidence to suggest that there exists a linkage between the enrichment of soil P beyond the agronomic optimum and dairying.

The New Zealand 2013-2014 milking season saw a national population of 4,922,806 dairy cows and total effective hectares under dairy (support blocks excluded) of 1.72 million hectares – an increase of about 40,000 ha on the previous season (Dairy NZ 2014). In New Zealand, dairy cattle graze on pastures for most of the year. However, in cooler areas such as southern New Zealand, poor pasture growth in winter requires an alternative strategy. Here, animals are typically placed in a field where pasture has been cultivated and a forage crop grown for winter feed. This is done to protect remaining pastures on the farm, but

results in dung deposition and soil disturbance when the soil is typically wet (McDowell et al. 2003).

Animal manure patches have been shown to provide an immediate and long term source of largely water soluble P, which can under the correct conditions can be transported by run-off or leached into soil (Chardon et al. 2007; Lucci et al. 2013). It has been found that the most abundant form of P in dairy dung was in the form of inorganic P (McDowell 2005; Hao et al. 2008). Inorganic P in the form of orthophosphate is also the primary constituent of most P fertilisers, when added to soil it is either sequestered into forms not readily available to plants or extracted from soil water into plants and microbial biomass (McLaughlin et al. 2011). Aarons et al. (2004) found that soil pH, EC, inorganic P and total P pools all increased and that as a function of the nutrients released, changed the soil properties under the dung pat.

The pool of organic P provided by manure or other high P organic amendments has the capability to move more rapidly through the soil profile. Dissolved organic P movement maybe enhanced through the soil profile by lack of sorption compared to inorganic P (Leytem et al. 2002). However, studies have shown that in some instances, sorption sites may not always be preferentially taken up by orthophosphates, but compete with organic anions for adsorption sites (Nziguheba et al. 1998; Malik et al. 2012).

This can create a greater risk of dissolved organic P transfer to groundwater. This shows that understanding the potential for P transport in areas receiving large applications of animal manures is difficult. There are many aspects related to manure composition and the forms of P contained in manures which can affect the potential sorption of P in soils and its potential for transportation.

McDowell et al. (2005) analysed the forms of P in sites receiving equal amounts of P from irrigated dairy effluent and in sites receiving only inorganic fertilizer. They concluded that more P was in the dissolved organic form for the irrigated dairy effluent site compared with the inorganic fertilizer site, which resulted in higher losses of P from the dairy effluent site.

1.7. Pathways of phosphorus loss

Although surface run-off is deemed to be the major pathway for potential P loss from pasture in the form of overland flow (Sharpley et al. 1992; McDowell et al. 2001), subsurface leaching of P has moved from being a subject that was poorly documented to a growing area of research, as seen by the rise in recently published works (Holman, Whelan et al. 2008; Djodjic et al. 2004; De Bolle et al. 2013; Gray 2015; McDowell et al. 2015).

This area of research is now leading to a closer investigation of differing soil types and their relationship with local geology and hydrological connections to surface waters (Carlyle et al. 2001; Kang et al. 2011).

The heterogeneity of the soil profile means that there is inherent difficulty in predicting the movement of mass (solids, liquids and gases) in the field situation, however to understand the mechanisms that lead to eutrophication of surface waters, there must be an understanding of the important pathways for P loss.

Hydrology determines the mode of transport that differing forms of P will take, during intense rainfall events of low frequency, P is moved as surface runoff, whereas low intensity rainfall of high frequency tends to move as subsurface flow. For P to be lost in subsurface flow it must first move downward (defined as leaching) below the soil surface either by matrix flow or by preferential flow in soil cracks, large pores vacated by dead plants or earthworm burrows (McDowell et al. 2001) (Figure 5).

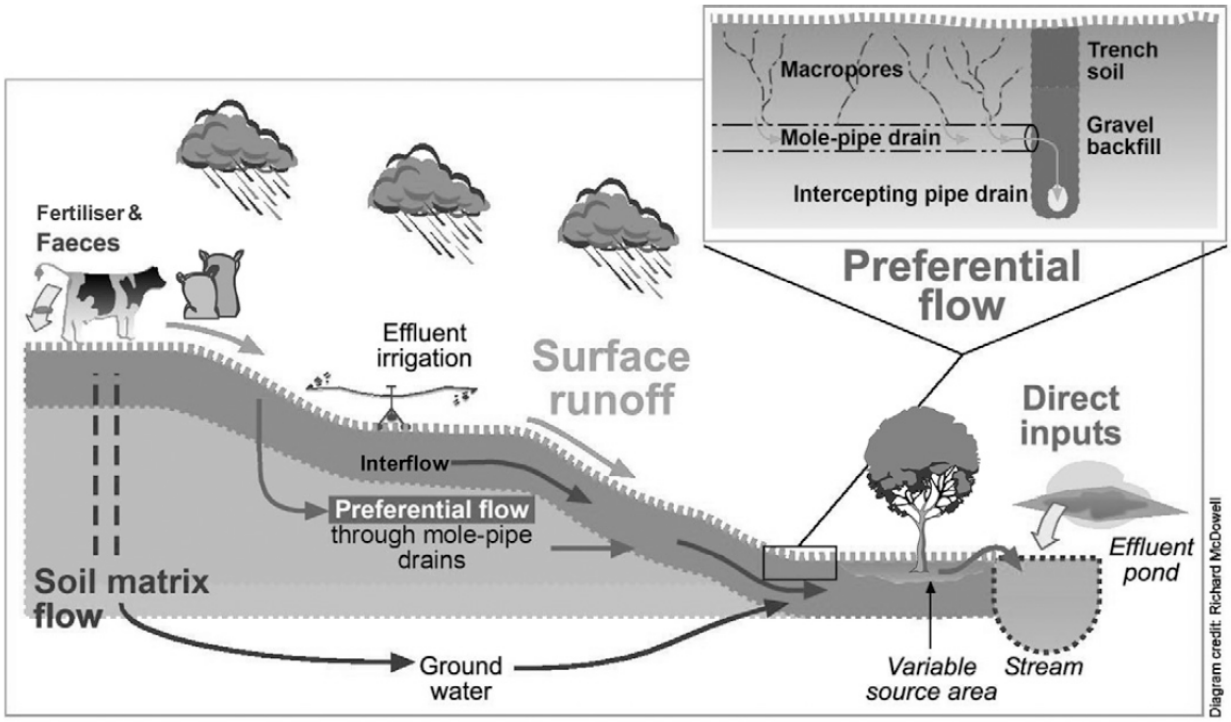


Figure 5: Conceptual diagram of potential sources and processes that transport phosphorus from the dairy pastures to surface water (McDowell et al. 2004).

1.7.1. Matrix flow.

Defined as the uniform downward movement of water through the macro-and micro pores of the soil. Contact time between solution and soil surfaces is measured in days and allows for P fixation by sorption sites within the soil matrix.

1.7.2. Preferential flow.

The movement of water with dissolved and suspended matter, preferential flow also moves downward in the soil but through the use of larger cracks, fissures, burrows and wormholes within the soil profile. Contact time is measured in minutes and hours and therefore there is less chance of P being adsorbed. Preferential flow increases transport of contaminants to surface waters and to groundwater and is seen as one of the most important pathways of P loss (Allaire et al. 2011).

The relative leaching vulnerability of different soils can be determined by the use of solute breakthrough curves where a solute tracer is applied to the soil surface then leached by rainfall or irrigation to measure the solute concentration over time. Soils with a higher

leaching factor will see the solute breakthrough much earlier (Carrick et al. 2014; Jarvis 2007). The use of dye and conservative tracers has aided in identifying the potential flow pathways involved in the fast transport of P via macro pores. These preferential flow pathways are important in that they have demonstrated the potential to bypass the buffering capacity of the upper layers of the soil profile (Gächter et al. 1998; Clothier et al. 2008).

The loss of P in subsurface flow has been shown to decrease as P comes in contact with sorption sites within the soil matrix, this however may not occur where organic matter together with low P-sorption capacity (sandy soils or gravels) where sub-surface flows travel from areas of high P to the unsaturated zone (McDowell 2012).

It has been identified that in order to minimise the risk of P leaching that there must a measure of control made on the amount of P that is applied to soils. Of the many methods available to minimise P losses to waterways from pasture, one simple approach is to ensure that soil test P concentration is maintained within the range that is considered optimal for pasture production (Edmeades et al. 2006; McDowell et al 2012). Having soil P above optimal levels is found to increase the risk of leaching (Monaghan et al. 2008).

However, even in farming systems where P application is seen to be in balance, can lead to the promotion diffuse loss of P. Kleinman et al. (2011) states that managing agricultural P to protect water quality may require adjustments to other conservation strategies. The non-tillage of soil was found to reduce P loss associated with particulate P, however the absence of tillage was found to aggravate the stratification of soil and residual P left over from fertiliser applications. This in turn concentrates applied P at the soil surface within the zone that contributes to the dissolved P loss.

1.8. Stony soils

Economic incentives of a high milk solid price has led to an increase in dairy herds and milking platforms in many areas of New Zealand. The conversion of lowland dry stock pastures into dairy units has been widespread in some of the most vulnerable leaching areas. Many of these areas contain glacial outwash fans and till deposits of gravels and sands covered by thin soil layers.

Alluvial gravels are particularly vulnerable to leaching as they are highly permeable and have sufficient preferential flow paths that allow for rapid transport of P, Studies in New Zealand are limited as are those from overseas, however research in stony soils has increased in recent years (Carrick et al. 2013; De Bolle et al. 2013; McDowell et al. 2013; Gray 2015). Recent work in New Zealand points to increasing P concentrations within sand and gravel aquifers underlying soils used for intensive dairy farming (McDowell et al. 2015).

Anion storage capacity (ASC) is a measure used to describe the P immobilisation potential of a soil. The conventional ASC test is expressed as the percentage of P that is removed from a solution of 1000ppm P by the soil after shaking at 4.6 pH, when the soil will exhibit maximum phosphate fixation. Soil ASC is categorised as High (<60%), Medium (30-60%), Low (<30%) (Saunders 1965).

Carrick et al. (2013), analysed significant land use change on stony soils since 2000. Analysis showed that 42% of stony soils have low ASC (<30%), 77% have moderate to rapid permeability, and 58% have low water storage capacity (30-90mm), attributes that all indicate high vulnerability to leach nutrients to surface water. Table 1, outlines broad groupings of New Zealand stony soils (Carrick et al. 2013). Stony soils (soil depth <45cm to gravels), that have potential for intensive land use (land less than 15° slope), are extensive with 1.68 million hectares mapped. 53% occur in Canterbury, 12% in Otago, with 9% each in Southland and the West Coast (Carrick et al. 2013).

Primary soil class	Very light	Light	Moderate	Slowly permeable	Poorly drained
					
Area	269 000 ha	384 000 ha	515 000 ha	285 000 ha	115 000 ha
Drainage class	Well drained	Well to imperfectly drained	Well to imperfectly drained	Well to imperfectly drained	Poorly drained
Profile available water to 1m depth	Very to extremely light (<60 mm)	Light (60–90 mm)	Moderate (90–120 mm)	Very light to moderate (30–120 mm)	Very light to moderate (30–120 mm)
P-retention	Low to moderate (<60%)	Low to moderate (<60%)	Low to moderate (<60%)	Low to moderate (<60%)	Low to moderate (<60%)
Permeability	Moderate to rapid	Moderate to rapid	Moderate to rapid	Slow	Moderate to slow
Representative soil families	Rangitata and Rakaia	Lismore and Eyre very stony	Lismore stony and shallow	Darnley, Lowburn, Ranfurly	Waterton, Dipton

Table. 1: Broad grouping of stony soils with the defining soil attributes. Carrick et al. (2013).

Carrick et al. (2013), in their investigation into the effects of intensive land-use, conducted scoping experiments into the leaching vulnerability of these young stony soils to a number of contaminants. Experiments were conducted with lysimeters under constant rate leaching of FDE and periodic irrigation with applications of superphosphate, cow urine and FDE. Results demonstrated a strong sensitivity to the application rate and depth of FDE, highlighting the critical management aspects and risks associated with these soils.

1.9. Purpose of this research.

The Otago Regional Plan: Water (Plan Change 6A), the purpose of which is to manage contaminant discharge and sediment from runoff, drains, leaching and earthworks, has established farm discharges limits in the Manuherikia river catchment of the Alexandra basin to be < 0.035 FRP mg/L by 2025.

Recent research conducted within the Alexandra basin of Otago, New Zealand, has highlighted conditions where the loss to groundwater of the potential surface water quality contaminant P, can occur. These are: high soil Olsen P concentrations, soils with low ASC (i.e. poor P sorption), and irrigation, which may regularly induce leaching to the vadose zone. If coupled with an unconfined aquifer– groundwater may become enriched with P and contribute to nearby connected surface waters (McDowell et al., 2015). One rich source of P is the dung from grazing dairy cattle. A review of regional trends in New Zealand has identified areas with high FRP concentrations of leachate P tended to have a high stocking rate and /or moderate to low soil P ASC, whereas those with moderate stocking density had high concentrations due to low P ASC in soils (Dymond et al. 2013).

It has been reported that dairy dung from gazing stock and FDE are both contributing to loads of FRP (Longhurst et al. 2000; O'Connor et al. 2001; Aarons et al. 2004; Lucci et al. 2013), However, FRP was quickly sorbed in soils of higher ASC, resulting in <4% of FRP in leachate (Toor et al. 2005).

The Alexandra basin area however, is typified by the presence of low ASC soils with high infiltration rates due to their lithology. McDowell et al, (2013) reported that subsurface losses of P were high compared to other farm scale losses under dairying in similar basin areas. Transport of contaminants including P to surface waters is most likely to be by irrigation-return flows via a combination of outwash, by wash, but most likely sub-surface flows. The low ASC of soils in the Alexandra basin were highlighted as a key potential cause of P loss.

There is a need for further research to investigate and model the pathways of P loss in low ASC soils given the extent to which this class of soil is being developed. There is a crucial requirement to determine the transport time for fertiliser P and effluent P applied to the surface of a low ASC soil to move down the soil profile and potentially into groundwater, particularly in the face of expected dairy growth within these regions.

The research objectives were chosen to study the potential for P to move down the vadose zone and into groundwater from common P applications under irrigated and grazed dairy pastures.

Research Objectives:

1. The bioavailability of different P forms in these gravels.
2. Do these areas of low ASC gravels coincide with enhanced vertical P loss?
3. How long would intensive farming of these areas take to enrich groundwater P?

Objectives 1 and 2 will be addressed with leaching studies utilising monolithic soil lysimeters and laboratory based leaching experiments, on soils taken from a recently established dairy unit that occupies part of the Manuherikia River flood plain in the Alexandra basin.

Objective 3 will be addressed using data gained from Objectives 1 and 2, in combination with data obtained from the Otago regional council (ORC) deep pan lysimeter situated on the Manuherikia River flood plain.

Chapter Two: Methodology.

2.1. Site description.

Lysimeters were collected in the spring of 2015 at 45° 05’40”S, 169° 37’57”E near the township of Omakau in the South Island of New Zealand (Figure 6). The study area landscape is described as semi-arid hill country with an irrigated low lying valley, characterized by terrestrial deposits from three distinct geological ages: lake and river sediments from a Pliocene conglomerate; and Quaternary/Pleistocene age outwash fans and alluvial deposits. The basin area is typified by the presence of low ASC soils. Agricultural practices are predominantly centred on sheep and beef farming, with a developing dairy industry.

The soil used for this trial came from a recently established dairy unit that occupied part of the Manuherikia River flood plain in the Alexandra basin. The farm was established in 2010 (270 ha) and supports a dairy unit operating with 3.2 cows/ha. This site was chosen as representing a potential high risk area for P loss to groundwater.

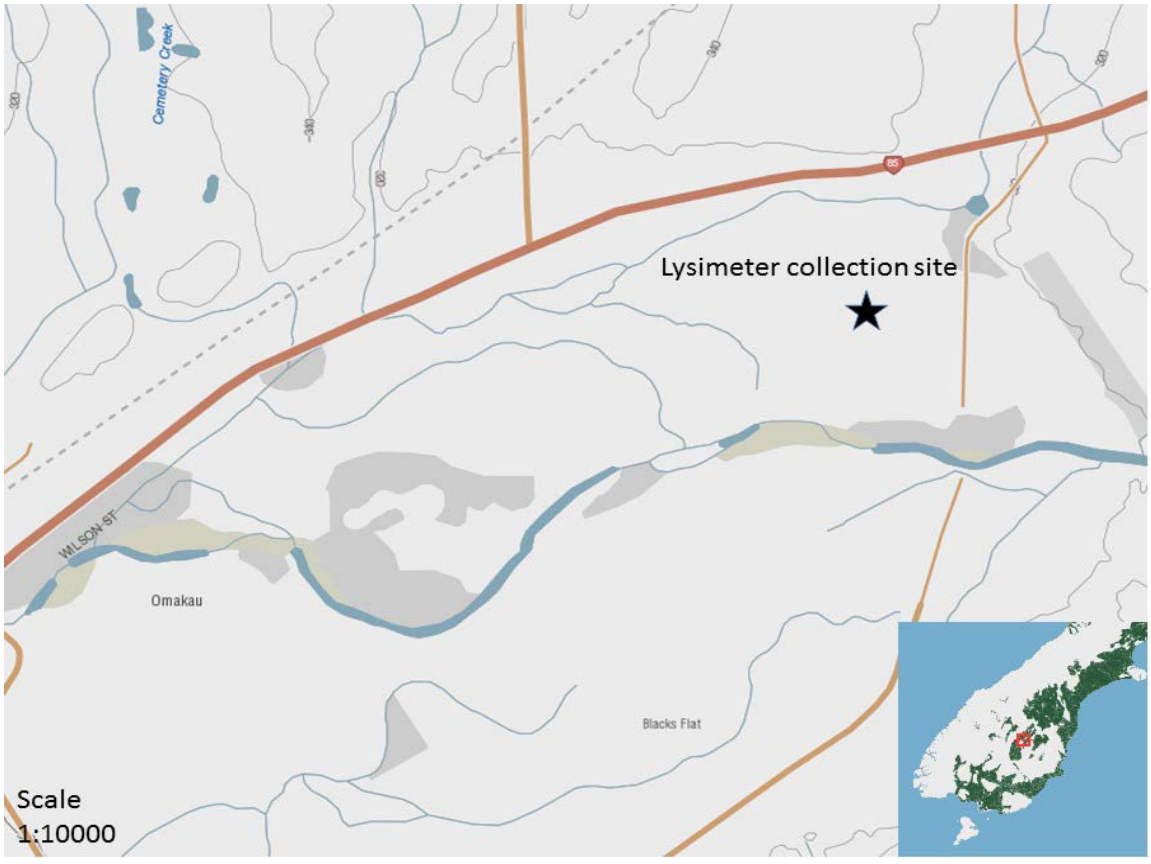


Figure 6: Lysimeter collection site. Source S-Map.

2.1.1. Groundwater hydrology.

Most of the available groundwater in the basin is contained within unconfined, water-table aquifers, which are primarily recharged by irrigation losses. These groundwater systems discharge their excess into the Clutha, lower Manuherikia or into the last kilometre of the Fraser Rivers. The aquifers are mainly high permeability sandy gravel systems, within glacial outwash of the Albert Town or Lindis advances. The base of these sandy gravel aquifers is generally defined by very low permeability silt and the mudstone beds of the Manuherikia group sediments. The collection site for the lysimeters sits above the Manuherikia alluvium or Manuherikia alluvial aquifer (Figure 7) and is defined by the flood plain of the Manuherikia River on its true left bank between the exit of the Ophir Gorge and Alexandra. This area, and the Quaternary alluvium within it, defines a shallow, unconfined aquifer in hydraulic connection with the Manuherikia River (ORC 2012), therefore the potential for P transfer to surface waters is increased.

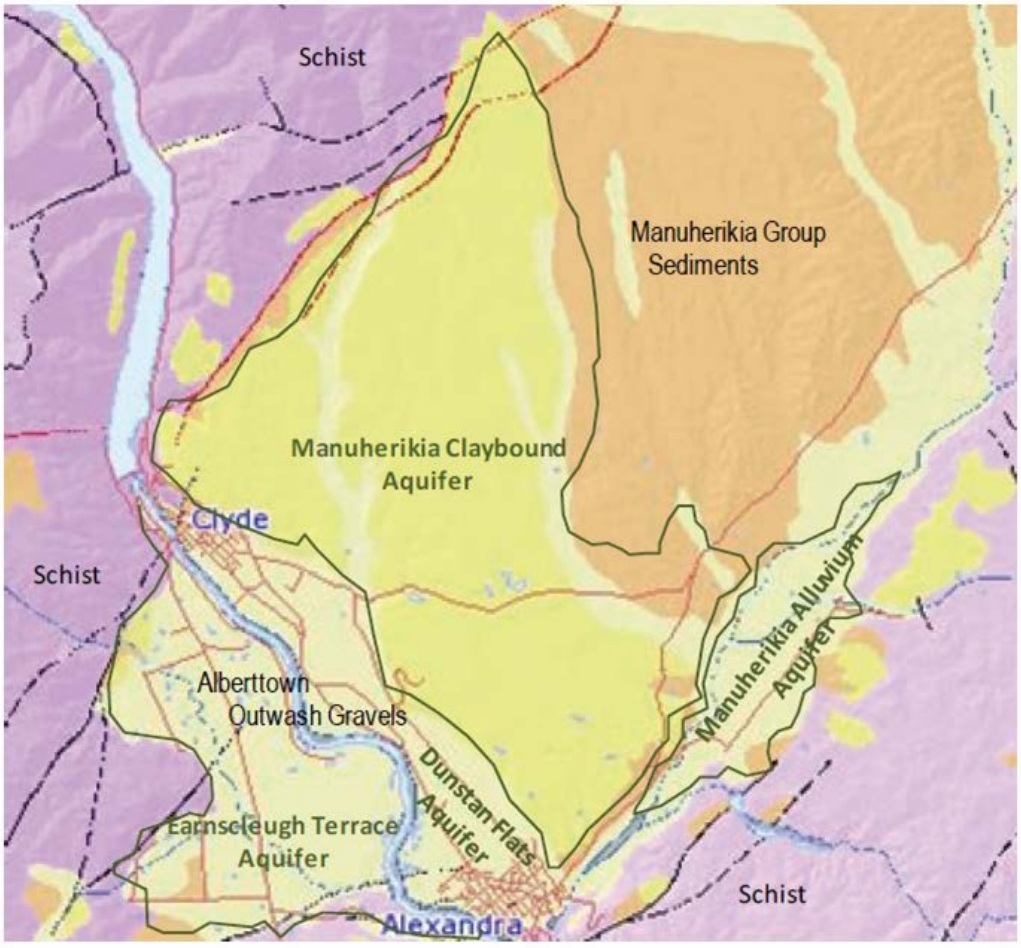


Figure 7: Alexandra Basin geology, Source ORC (2012).

2.1.2. Soil key physical properties.

Soil key physical properties were examined prior to the excavation of Lysimeter cores. At the closest resolution 1:10000 scale provided by Landcare Research based S-map, the dominant soil class is displayed as an Orthic Gley Soil (Flaxton*f*), however a paddock scale examination of the soil layers revealed a closer relationship to the adjacent Rangitata*f* soil class described as a Fluvial Recent soil. It was therefore decided to base the key soil properties upon the closest relationship. Information contained in Table 2.1 is based on available data from S-Map soil reports and details key properties of the dominant Rangitata*f* soil class. This provides an overview of the soil class, detailed analysis of paddock scale finding are included in the results.

Table 2.1: Soil key physical properties.

Key physical properties	
Depth class (diggability)	Very Shallow (0 - 20 cm)
Texture profile	Sandy Loam
Potential rooting depth	Unlimited
Rooting barrier	No significant barrier within 1 m
Topsoil stoniness	Moderately stony
Topsoil clay range	0 - 8 %
Drainage class	Moderately well drained
Aeration in root zone	Unlimited
Permeability profile	Rapid
Depth to slowly permeable horizon	No slowly permeable horizon
Permeability of slowest horizon	Rapid (> 72 mm/h)
Dry bulk density, topsoil	1.18 g/cm^3
Dry bulk density, subsoil	1.38 g/cm^3
Depth to hard rock	No hard rock within 1 m
Depth to soft rock	No soft rock within 1 m
Parent material origin	Alluvium
Depth to stony layer class	Shallow
Topsoil P retention	Low (19%)
N leaching vulnerability	High
Structural vulnerability	Very high

Particle size distribution of mineral fines was analysed by the Otago University geography Laboratory using a Malvern Mastersizer, Hydro 2000G with a Malvern autosampler 2000 attachment, with an added de-flocculation agent of Sodium Hexametaphosphate to prevent particles clumping together and being read as one large grain.

2.1.3 Lysimeter collection site

At the paddock scale the collection site consists of a dairy pasture containing a mixed clover/ryegrass sward, gently undulating and sloping towards the Manuherikia River. Irrigation is currently undertaken with a travelling irrigator also supplying FDE at a low rate application (Figure 8). The location for the excavation of the lysimeters was selected to avoid irrigator tracks and areas of high traffic to avoid areas of compaction. Areas of obvious urine or dung deposition were also avoided to limit differences between treatments. The pasture receives a maintenance N and P fertilizer rate of 200 and 45 kg N and P/ha/yr, respectively.

Soils across New Zealand have been classified by Landcare Research Ltd and AgResearch Ltd into high and low soil risk categories for FDE application. A soil risk decision tree has been developed with 5 risk categories, High Risk (A, B, C) and Low Risk (D, E). The Rangitataf soil class is defined on the scale as low risk (E) being well drained but very light flat land (< 7 degrees). With a very stony sandy layer within 300 mm depth. This risk factor limits the applied irrigation to prevent loss of effluent to the environment.

Figure 8: Lysimeter collection site.

This location has also been used by the Otago regional council (ORC) to investigate nutrient loss to the soil profile. From 2011 to 2014 a deep pan lysimeter was operating to collect data to inform on the nitrogen leaching potential (Figure 9). The site is underlain by a permeable aquifer – 2.3 m saturated thickness. Hydraulic conductivity = 2600 m/d (3 x 10-2 m/s) and the depth to water table was 2.9 m. Irrigation is applied through a centre pivot and effluent applied from the irrigator was crossing the lysimeters one – two days a month Dec – May. Cows grazed in the paddock with the lysimeter roughly 4 days each month (ORC data). Data obtained from the ORC deep pan lysimeter was used to compare and inform hypotheses in conjunction with results from monolithic lysimeters trial and column experiments conducted at Invermay Research Farm.

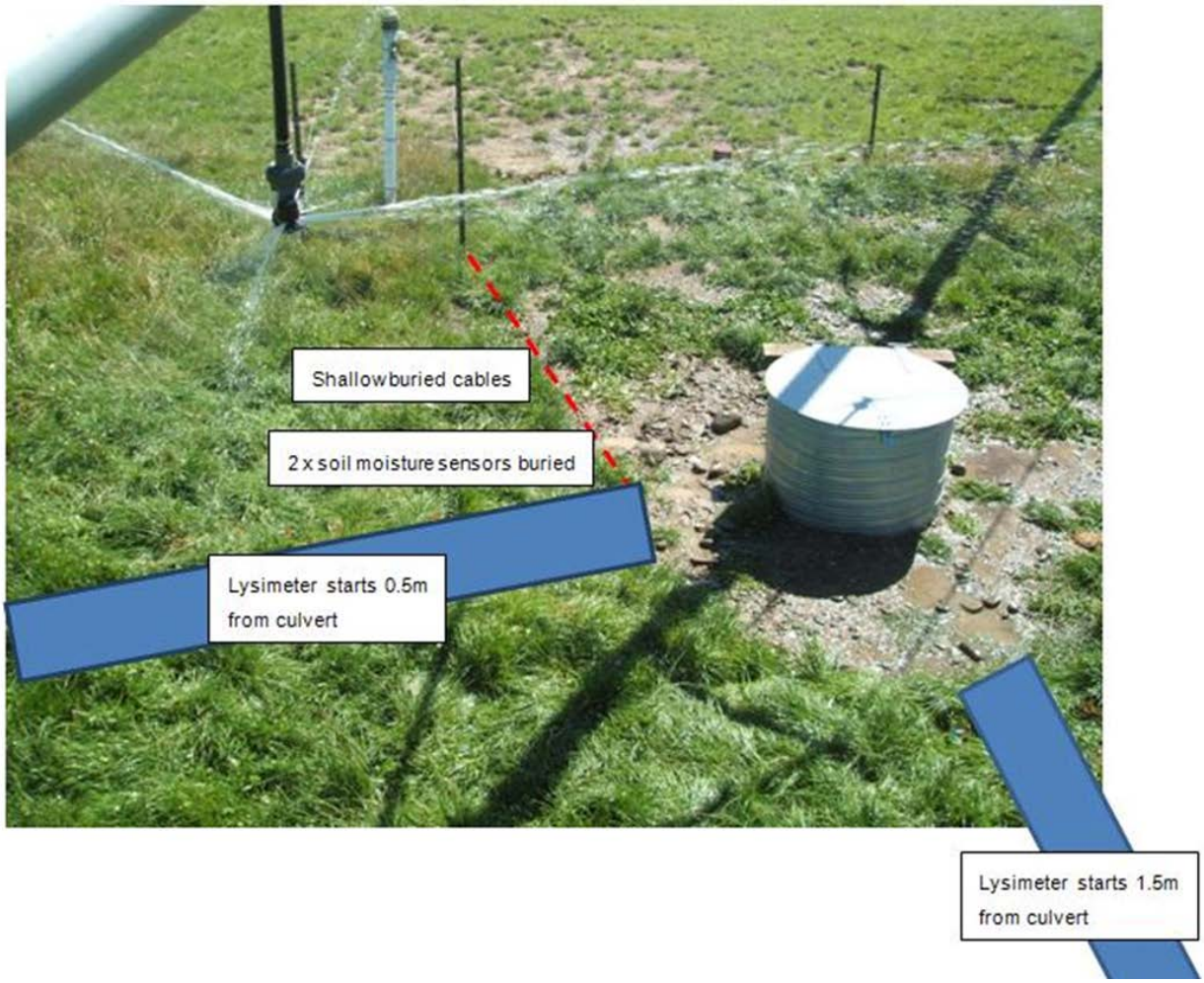


Figure 9: Otago regional council Lysimeter site.

2.3. Lysimeter trial.

A lysimeter approach to measuring the transport and leaching losses of solutes was deemed the best approach to enable the measurement of near to real-life conditions within the soil profile whist allowing easily accessible measurement to be taken. During the spring of 2015, 48 Lysimeters were excavated from the dairy site and prepared for removal and transport to a purpose built lysimeter farm at the Invermay Research Campus located near Dunedin. The decision to base the conduct of the trial at a differing location to the collection site was based upon the distance that would be required to service in-situ lysimeters and the ability to install the lysimeters at a facility that was able to quickly process samples in response to leaching events.

Collection of the lysimeters followed the method outlined by Cameron et al. (1992). A monolithic gravimetric lysimeter design was used with monoliths of 30 and 50 cm depths, excavated within a 300mm PVC pipe, giving a surface area of 708 cm^2. Lysimeters were excavated from the pasture by steel cutting tool and hand calving, the edges were then sealed with molten petrolatum to reduce the occurrence of edge flow. Monoliths were then capped with plywood top and bottom and bolted together to minimise disturbance during transport (Figures 10 and 11).

Figure 10: Lysimeter excavation site.

Figure 11: Calving and transport of monoliths form excavation site.

Upon return to Invermay campus the bottom cap was removed and the space between the soil and base cap was then filled with acid washed sand to fill any voids and allow for freely draining seepage collection. The space between the monolith and side wall of the casing was again checked for void spaces and petrolatum added in necessary. Lysimeters were then equilibrated outside at the Invermay research station for 2 weeks prior to installation in a pre-fabricated lysimeter trench and attached to 1000ml collection containers (Figure 12). A WatchDog Model 2700 weather station was installed alongside the lysimeter trench to measure rainfall, relative humidity and temperature with an additional manual rain gauge as a secondary reserve.

An automatic metered irrigation system consisting of Gardena T1030D control unit connected to farm water supply was installed above the lysimeters, this was then fitted with individual adjustable mirco spray nozzles above each lysimeter with a spray shield to limit wind drift leading to irrigation loss. Trial runs of irrigation timing and volume were conducted to ensure an even irrigation rate across all lysimeters and then matched to volumes out of the collection containers to confirm the absence of edge flow.

Before the application of treatments, 50mm of irrigation water was applied over 2 weeks. Leachate was then collected and analysed for baseline concentrations of FRP and Total Phosphorus (TP).

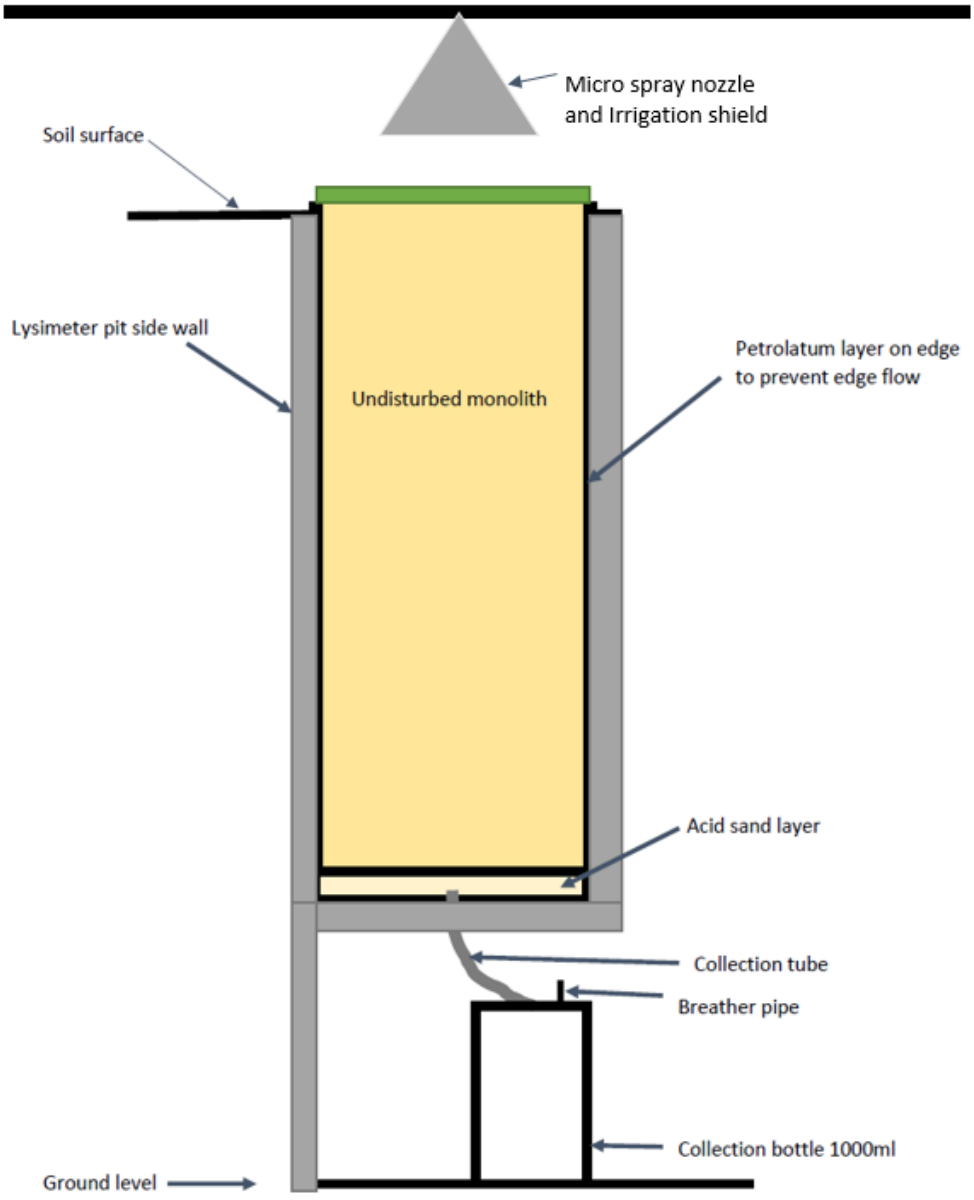


Figure 12: Diagram of lysimeter design.

Lysimeter bays were located in a farm pasture block adjacent to the research campus and were isolated from stock interference and local hydrology.

Dung was first analysed to determine nutrient content before application, the dung was collected the day before application and analysis was conducted by Eurofins overnight. Each dung application was weighed to 2kg (based on P content vs load required for 50kg/ha P), prior to placing on the lysimeter Table 3.3a displays characteristics of dung applied to lysimeters.

Table 2.3a: Properties of Dung applied to lysimeters.

Dung	N† %	P† %	Cl† %	TC† %
	0.59	0.13	<0.1	7.7

†Indicates: g/100g

Leachate was collected from the lysimeters after events or when drainage equalled 1 litre. Irrigation was applied on a daily basis from the end of October 2015 to February 2016, after which time collection was carried out on an event only basis. This was due to cost restrictions of time and processing of laboratory samples. Therefore cumulative drainage may be under estimated.

Treatments were applied on the 29th of October 2015 and consisted of those common concentrations and forms of P lost in leachate from P applications, under irrigated and grazed dairy pastures. The aim being to provide data to better understand the potential for P to move down the vadose zone and into the groundwater.

Each depth (30 cm and 50cm) had 6 replicates of 4 treatments consisting of:

- Control (no P).
- Superphosphate (50 kg P ha).
- Dung (dairy at 50 kg P ha).
- Superphosphate + Dung (100 kg P ha).

Figure 13: Lysimeter dung treatment at time of application.

Dung used in the treatment was sourced from a local dairy farm running a similar feed regime to the Omakau site, with a mixed sward of clover/ryegrass. Dung was sourced from a pasture grazed no longer than 24 hrs earlier by dairy cattle and sent for overnight analysis of nutrient content by a commercial lab prior to application.

The application of dung treatments to the lysimeters used a steel ring to contain the dung within the lysimeter until it could stand unassisted, thereby retaining the P load intended for the lysimeter (Figure 13). Each dung application was weighed to 2kg (based on P content vs load required), prior to placing on the lysimeter.

Superphosphate was supplied by Ballance Agri-nutrients Ltd as a single superphosphate and trial application rate was calculated from the product P content equated to the surface area of the lysimeter. Each application was weighed and placed into labelled containers ready for treatment application (Figure 14).

Figure 14: Superphosphate treatment at time of application.

Irrigation water (480 mm overall) was applied from Oct 2015 to April 2016 by metered application of 3mm per day, which together with natural rainfall over this period delivered 800 mm of total irrigation.

2.3.1. Lysimeter sampling.

At start of the trial, soil was sampled at 10 locations within the dairy pasture, near the lysimeters excavation site and from 0-7.5, 7.5-15, 15-30, 30-40, 40-50 cm depths. This was then analysed for ASC, Olsen P, water extractable P and pH.

ASC was determined using the P concentration remaining in solution measured colorimetrically via reaction with nitric vanadomolybdate acid reagent (Kitson et al.1994).

Olsen P was measured by extracting air dried soils in a 0.5 M sodium bicarbonate solution at 8.5 pH for colorimetric analysis (Olsen et al 1954).

Water extractable P provides a direct estimate of the potential FRP loss to surface waters, therefore following the methods of McDowell et al.(2004), air dried samples of 0.50g (> 2 mm well homogenised) soil were added to 150ml of RO water and shaken for 45 min. Filtered (< 0.45 µm) and P concentration determined colorimetrically by the Murphy Riley method.

Leachate was sampled in response to natural rainfall events (> 5 mm) and weekly (whichever was the more frequent). There were cost limitations on the amount of laboratory analysis that could be conducted, therefore sampling after the first few weeks of initial activity in the lysimeters was based on responding to significant rainfall events, whilst continuing to monitor the performance of the trial site.

Total volume of leachate per event was recorded during collection and the filtering of samples was conducted during collection. Leachate was filtered with a < 0.45 µm glass fibre syringe filter and FRP, TP and Total filterable P determined colorimetrically using the method of Watanabe et al.(1965) on a T80+UV/VIS Spectrometer at the 712nm range +/- 2µm.

Soil Total P was conducted by perchloric acid digestion (Sommers et al.1972). 0.20g (> 1mm, well homogenised) soil in glass digestion tubes were left overnight in fume hood to oxidise the organic matter. The following day 250µl $MgCl_2$ was added to each tube and digested at 80°c for 30 mins. Once cooled, 3ml perchloric acid was added to each tube and placed back on digestion block and gradually increased to 210°C until soil residue turned white and the solution was clear. It was then allowed to cool before samples were then diluted to 50 ml with RO. Samples were filtered with GFA grade filters before colorimetric analysis.

Sub-samples (unfiltered) of 70ml were retained for persulphate digestion, and the remaining sample bulked in 5 litre containers according to treatment and depth, for later use in the column experiment, these samples were then stored in a 2.0°C until required.

At the conclusion of the trial, the lysimeters were destructively sampled and again and the same criteria measured to determine changes in soil characteristics.

2.4. Column experiment.

To investigate the attenuation and transport of differing P compounds in the gravel aquifer media, we conducted a series of column experiments. Column experiments were used as a time and cost effective means of providing BTC (breakthrough curves) to estimate parameters of physicochemical processes in the substrate. Column trials were conducted from 0ctober to November 2015 at the Invermay campus.

Gravels used in the experiment were sourced from the same location as the Lysimeter trial but at a depth of 1-2m below the plough layer. Gravels were then air dried at Invermay campus and sieved to 8mm to allow for packing into small columns of 300mm x 75mm, giving a volume of 1325.3 cm^3. Columns had a 3mm hole drilled into the concave base to allow for drainage and were fitted with 1mm fine mesh and material voil covering to limit small fines from entering the leachate. Columns were saturated for 24 hours in Reverse osmosis (RO) treated water to fill pore space, thereby limiting the occurrence of preferential flow, and allowed to drain for 1 hour prior to treatments being applied.

Treatment solutions of 1 litre were prepared the day before application to a 2 ml/g concentration and refrigerated overnight. Before application, solutions were brought up to room temperature of approximately 18°C. All treatment solutions were injected manually by syringe evenly across the tops of the columns at a rate of 200ml/hr and leachate collected, filtered and analysed the same day for FRP and TP. A simple bench top system was constructed for the columns, attached to supporting stainless steel rods that allowed for the collection of leachate into graduated collection containers (Figures 15 and 16).

Columns breakthrough curves of organic P compounds were examined for species behaviour and compared to orthophosphate (as KH_2PO_4) as an indication of mobility. All columns used in the experiment were first rinsed with RO and dried before packing and every effort was made to ensure the same packing consistency was maintained between

columns. Columns were not reused between treatments to eliminate contamination risk.

Figure 15: Column experiment arrangement.

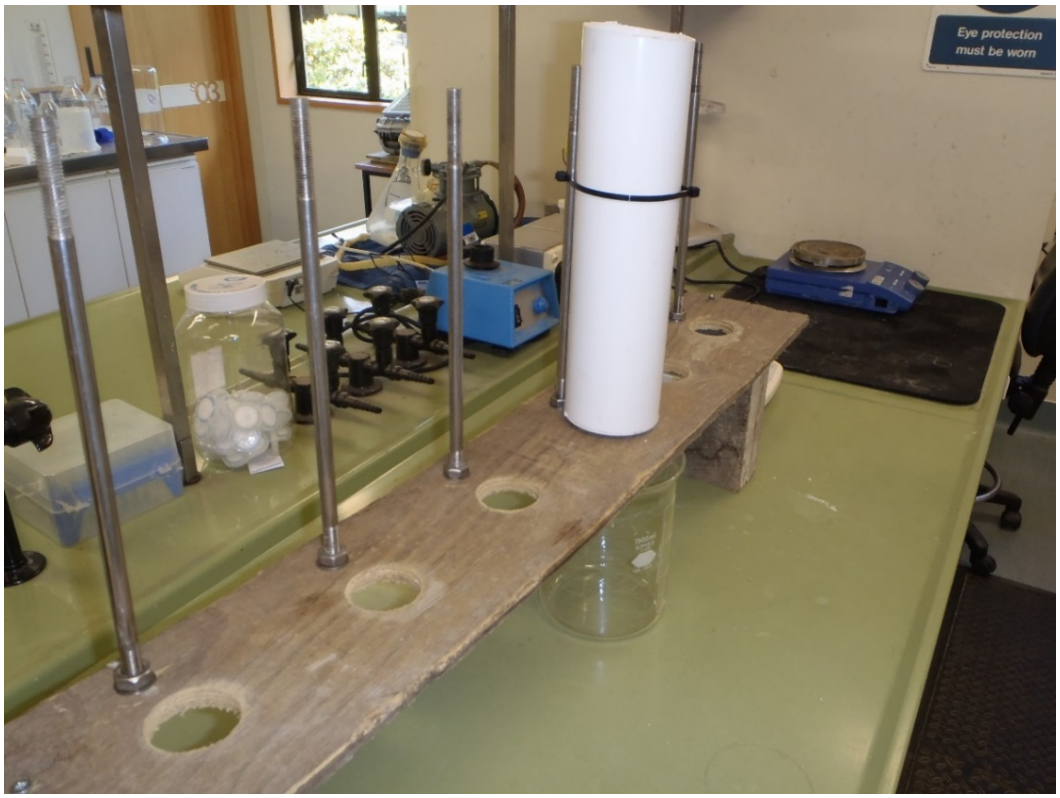


Figure 16: Column experiment setup.

Treatments included were a non-reactive KBr tracer at 1 mg Br/L and (largely organic) P compounds of Phosphocreatine, D-glucose 6 phosphate, D-glucose 1-phosphate, 4-nitrophenyl, Adenosine, Bis p-Nitrophenyl phosphate, Phytic Acid, Guanosine-Monophosphate, n-(phosphonomethly)glycine 9, Potassium dihydrogen , Lecithin, o-phospho-6-serine (all 2 mg P/L). These compounds were used to represent a range of monoester and diester P.

In addition to the organic P compounds, leachate collected from the dung treatments of the lysimeter trial was applied to column, with and without a bromide tracer. Concentrations of the KBr tracer were recorded during the column runs with a Thermo scientific Orion Star meter with attached solid state Ion selective electrode probe to indicate a relative steady flow state of the solute. Sub-samples of the leachate collected and retained in a chiller, for use in column trial treatments were analysed for FRP and TP prior to use in column experiments.

Samples were taken at 10 min intervals until two pore volumes were leached. Due to the amount of samples generated and time involved in analysis, it was decided to run the treatments through in groups of 6. This allowed for the analysis for FRP and TP to be completed the same day, by colorimetric analysis.

2.5. NaOH-EDTA extraction and ^{31} P nuclear magnetic resonance spectroscopy (^{31} P NMR).

To determine the organic P species leached from the lysimeters a sample of dung leachate was analysed by ^{31} P nuclear magnetic resonance spectroscopy (^{31}P NMR).

A 5L sample of dung leachate collected from the lysimeter trial, was freeze dried down to 2.2g in preparation for extraction. The freeze dried dung leachate sample was shaken in 40 mL of 0.1M NaOH + 0.05M Na-EDTA for 2 hrs. Then filtered through a small GF/A filter paper. A subsample of 0.1mL was taken and diluted to 10mL, this was then analysed for reactive P and total P. The remaining 39.9mL was frozen and freeze-dried, in preparation for (^{31} P NMR) analysis.

Analysis was conducted by the Otago University chemistry department. ^{31}P NMR spectra were obtained using a Varian 500MHz Inova NMR spectrometer at 25°C. Shimming (z1-z4) was performed manually using the shape of the water line in the 1H spectra of the sample. A Varian 10mm Broadband probes was used. Samples were locked on the D2O and run at 202.298 MHz, at 20oC, with a spectral window of 12247 Hz, using 65536 data points. Chemical shifts were recorded relative to an external phosphoric acid standard (δ = 0 ppm) in a capillary tube. Samples were prepared to a pH > 13 by taking 1 g of the dried extract, adding 3mL of D2O and 500 µL of 10M NaOH. Samples were ultrasonicated for 3 min, equilibrated for 20 min, and then centrifuged.

2.6. Laboratory analysis.

Lab analysis was conducted at the Invermay research campus where practical, during the course of the trial work, with limited use of outside analytical services. This analysis provided data for the statistical analyses and examination of the potential risk of impact on aquifer-P concentrations.

2.7. Quality control

To avoid contamination, all samples were filtered through new glass fibre syringe filters into unused sterile containers. All glassware used in digestions and colorimetric work was washed in 0.25 M sulphuric acid followed by distilled water between sample runs.

Quality control of samples included reagent blanks and blank samples for each analytical run, with 10% of the total samples run as duplicates. Calibration standards were first run to ensure instrument performance. Calibration standard curves were calculated from absorbance vs P concentration using linear regression to calculate the P concentration in each sample for the measured absorbance.

2.8. Statistical analyses and modelling.

Statistical analyses was conducted using Genstat 18th Edition to examine analysis of variance of log transformed data, examining treatment to treatment interaction factoring in date, depth and treatment. Minitab 17.81 was used for confirming the normal distribution of background lysimeter results, Grubb's outlier test and further ANOVA analysis of main effects of treatment and date.

Research questions are addressed via a mass balance table of inputs and the empirical relationships from data generated and validated against in situ lysimeter and stream flow concentration data generated by the Otago Regional Council using a combination of simple yield coefficients for leaching losses by dairying from top and subsoil calibrated against lysimeter data from the Otago Regional Council to 2-m depth and the likelihood of transport through gravels.

Chapter Three: Results

3.1. Soil physical properties

Results are presented for the key soil physical properties of the lysimeter collection site at Omakau, Central Otago. Background as well as post-trial soil chemistry data is reported for pH, Olsen P and Total P. The Key results of soil analysis are presented in tables 3.1a to 3.1d. Full soil results are presented in the Appendix.

Table 3.1a: Background soil analysis results for the lysimeter study undertaken in October 2015, prior to trial treatment application.

Depth	pH	Olsen P mg/kg	Total P mg/kg
0-10 cm (n=10)	6.14 (0.10)	25.6 (3.8)	818.0 (55.4)
10-20 cm (n=10)	6.26 (0.05)	14.2 (2.5)	663.3 (61.1)
20-30 cm (n=10)	6.42 (0.24)	11.2 (2.8)	546.2 (63.8)
30-40 cm (n=10)	6.66 (0.36)	8.8 (4.9)	428.5 (87.6)
40-50 cm (n=10)	6.72 (0.38)	8.5 (4.6)	417.6 (51.7)

Brackets denote the SE of the Mean.

Table 3.1b: ASC% by Potassium dihydrogen phosphate buffer prior to start of lysimeter trial.

Depth	Anion storage capacity (ASC) %
0-10cm	6
10-20cm	7
20-30cm	6
30-40cm	6
40-50cm	5

ASC is lower than reported by the soil class description given by S-Map (19%).

Table 3.1c: Results are displayed for particle size analysed by the Otago University geography Laboratory, from sampling of trial site from 10 cm to 50cm depth.

Depth cm	% GRAVEL:	% SAND:	% MUD:	% Clay
0-10 cm	0%	70.70%	29.20%	0.002%
10-20 cm	0%	63.90%	36.06%	0.004%
20-30 cm	0%	54.24%	45.74%	0.007%
30-40 cm	0%	68%	31.99%	0.005%
40-50 cm	0%	76.26%	23.73%	0.003%

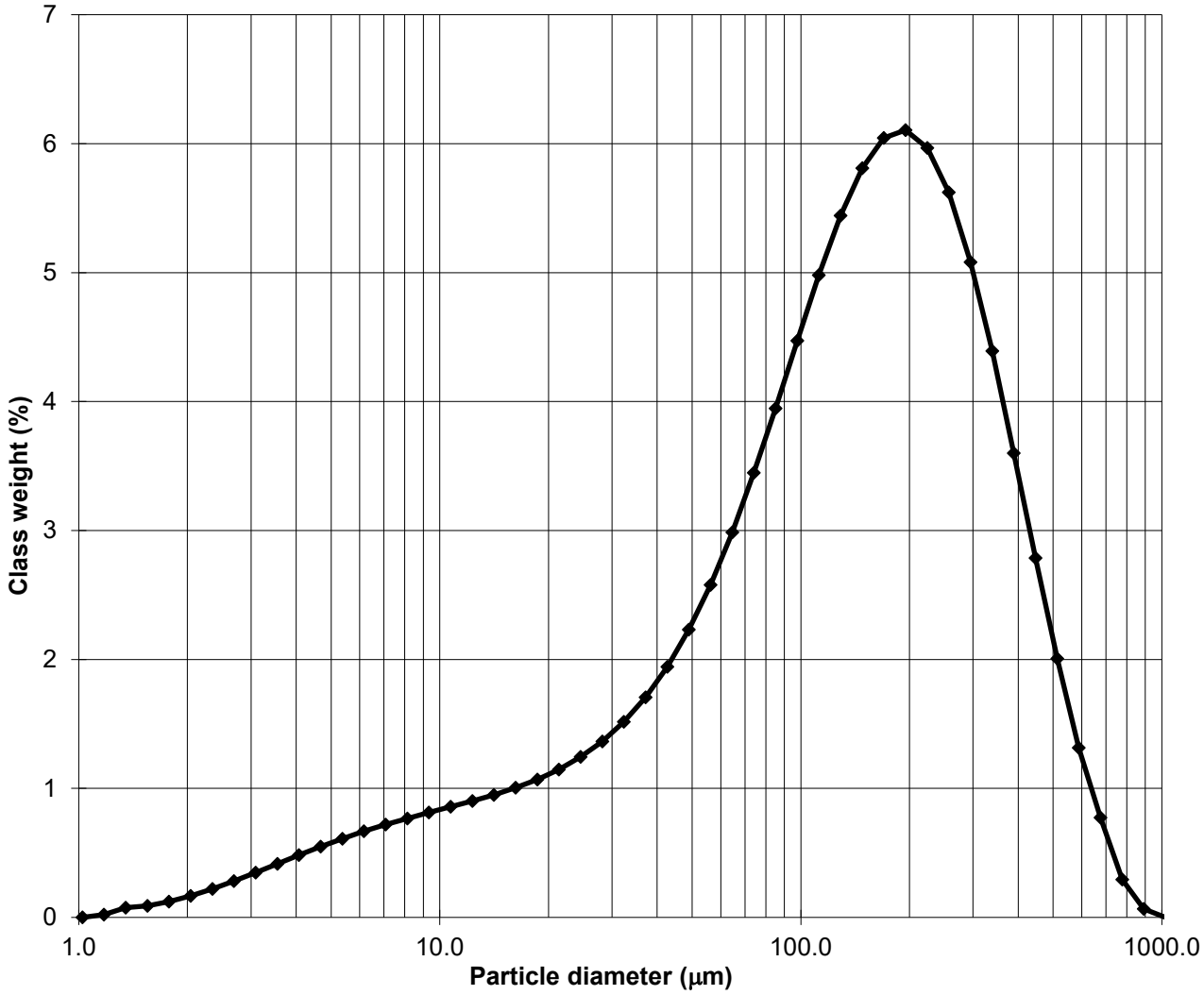


Figure 17: Particle size plotted against the logarithm of effective particle size shows a frequency distribution curve that indicates the Sand fraction as the dominant particle size contained within the background soil samples from the lysimeter collection site.

Results of particle size analysis are displayed in the Ternary diagrams of Figures 18 and 19 and give an illustration the proportions of sediments found. Textural groups of samples to 50cm depth ranged from Sand-muddy Sand to Sandy mud. Sediments were identified as ranging between Poorly Sorted Medium Sand to Very Fine Sandy Very Coarse Silt.

Figure 18: Ternary diagram of Sand to Mud proportions.

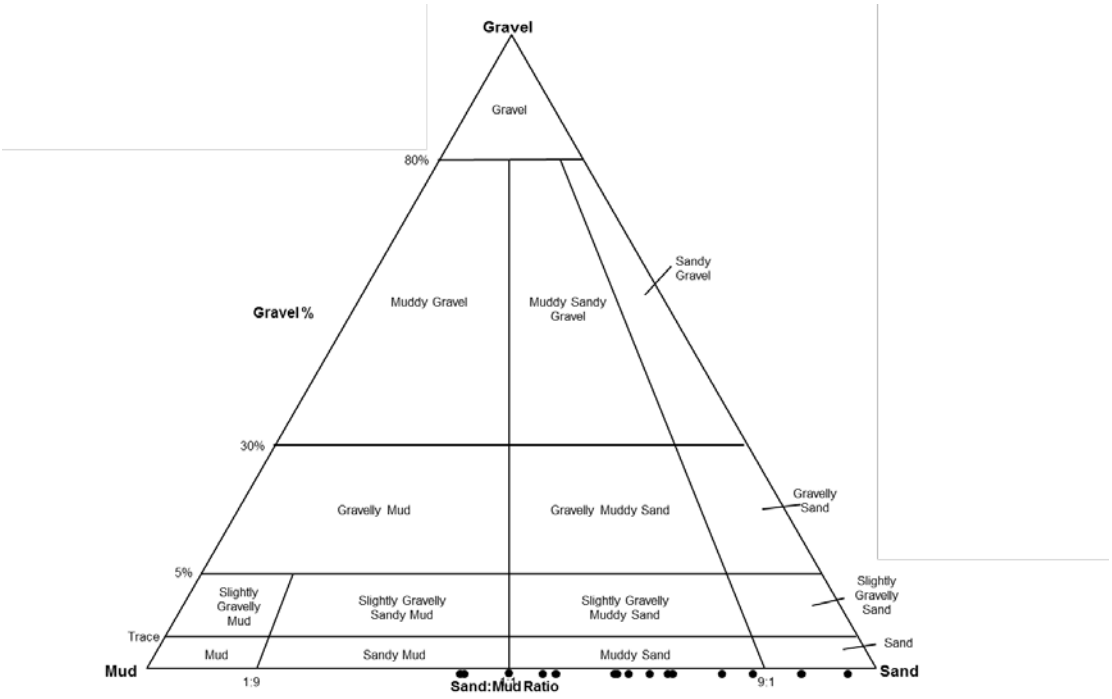


Figure 19: Ternary diagram of Silt to clay proportions.

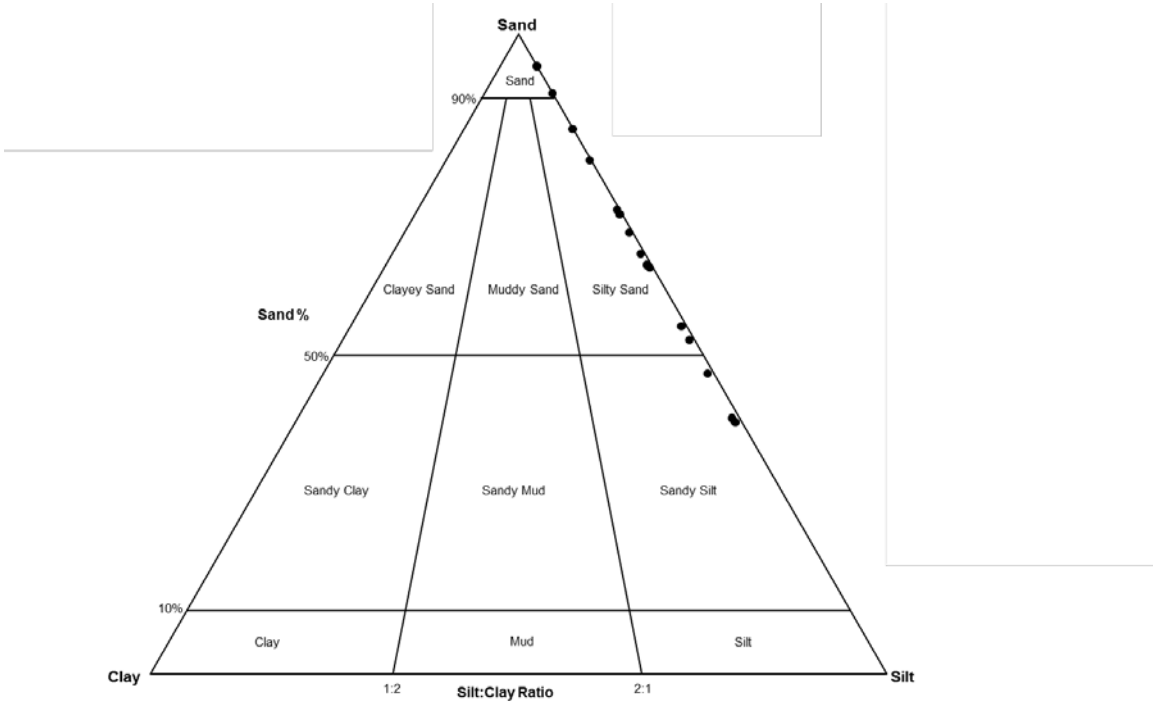


Table 3.1e: Lysimeters were destructively sampled at the end of the trial to determine changes in the soil chemistry. Results are displayed for samplings of post-trial soil chemistry undertaken in April 2016.

Depth	Treatment	Olsen P (mg/kg)	WEP P (mg/L)	Total P (mg/kg)
0-10 cm	Control	6.0 (0.06)	0.06 (0.01)	682.1 (12.0)
10-20 cm	Control	4.3 (0.17)	0.047 (0.004)	651.0 (15.8)
20-30 cm	Control	3.2 (0.26)	0.045 (0.006)	574.9 (12.5)
30-40 cm	Control	2.7 (0.50)	0.041 (0.001)	845.0 (273)
40-50 cm	Control	2.7 (0.24)	0.039 (0.005)	526.5 (24.0)
0-10 cm	Dung	15.0 (1.79)	0.100 (0.004)	792.7 (22.7)
10-20 cm	Dung	5.2 (0.81)	0.054 (0.005)	644.0 (27.0)
20-30 cm	Dung	3.7 (0.59)	0.054 (0.008)	543.8 (33.0)
30-40 cm	Dung	2.9 (0.59)	0.047 (0.004)	363.9 (64.6)
40-50 cm	Dung	2.3 (0.41)	0.043 (0.004)	516.1 (37.4)
0-10 cm	Super	5.5 (1.07)	0.062 (0.003)	744.3 (18.0)
10-20 cm	Super	4.1 (0.46)	0.050 (0.004)	748.0 (190.0)
20-30 cm	Super	3.1 (0.5)	0.046 (0.006)	657.9 (72.2)
30-40 cm	Super	2.7(0.65)	0.049 (0.006)	595.6 (50.9)
40-50 cm	Super	2.7 (0.17)	0.047 (0.005)	536.8 (45.20
0-10 cm	Super + Dung	12.7 (1.83)	0.086 (0.006)	827.3 (59.9)
10-20 cm	Super + Dung	5.1 (0.35)	0.055 (0.002)	672.0 (156.0)
20-30 cm	Super + Dung	3.9 (0.24)	0.052 (0.004)	568.0 (49.0)
30-40 cm	Super + Dung	3.7 (0.29)	0.047 (0.005)	481.5 (56.9)
40-50 cm	Super + Dung	3.1 (0.26)	0.042 (0.007)	443.5 (29.9)

Brackets denote the SE of the Mean.

3.2. Climate.

General climate conditions were favourable. Annual temperatures were above average (0.51°C to 1.20°C above the annual average) throughout the trial period.

Rainfall was near normal (within 20% of the annual normal) expected within the Lysimeter trial site, with a recorded 303mm of precipitation. No major rainfall events during the period of the trial.

Rainfall for the period of the 28th October 2015 to end of March 2016 is shown in Figure 20. Moderate rainfall events were recorded on the 26th November 2015, with 32mm occurring and again on the 13th and 26th of January 2016 with 24mm falling and 19mm respectively.

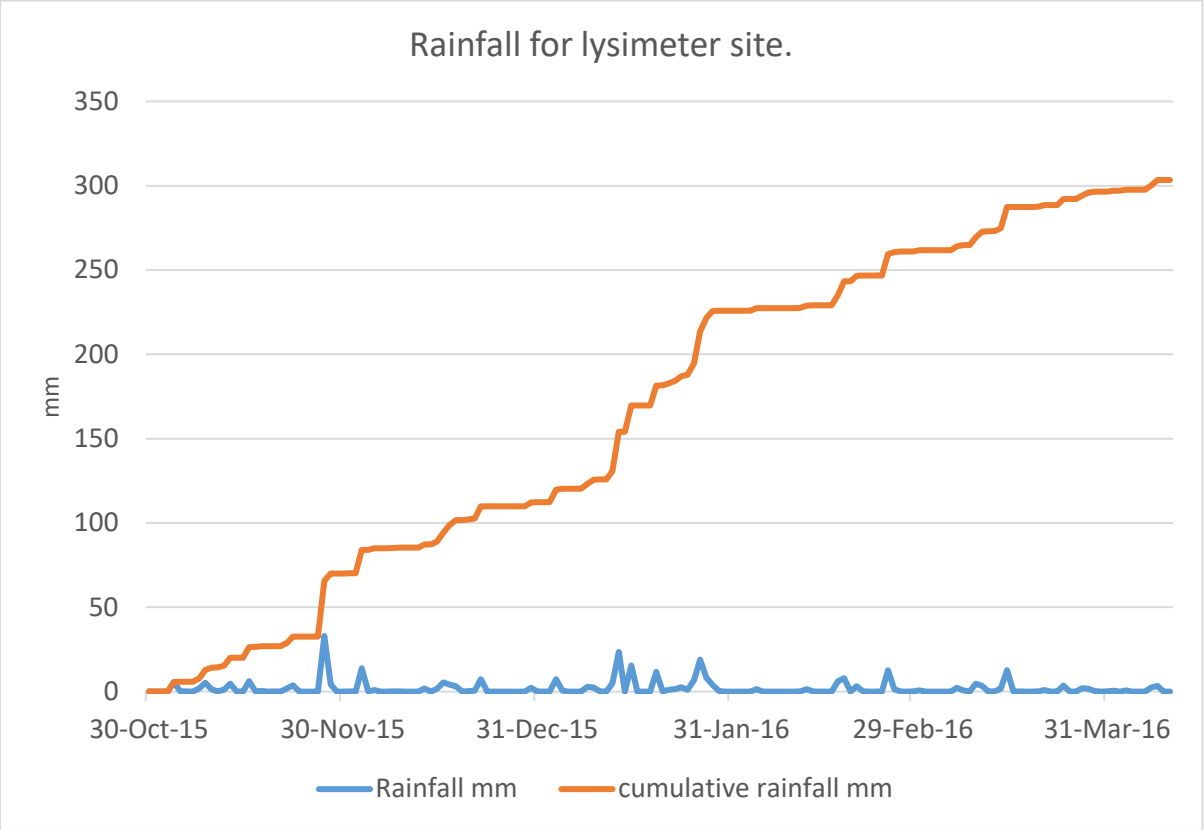
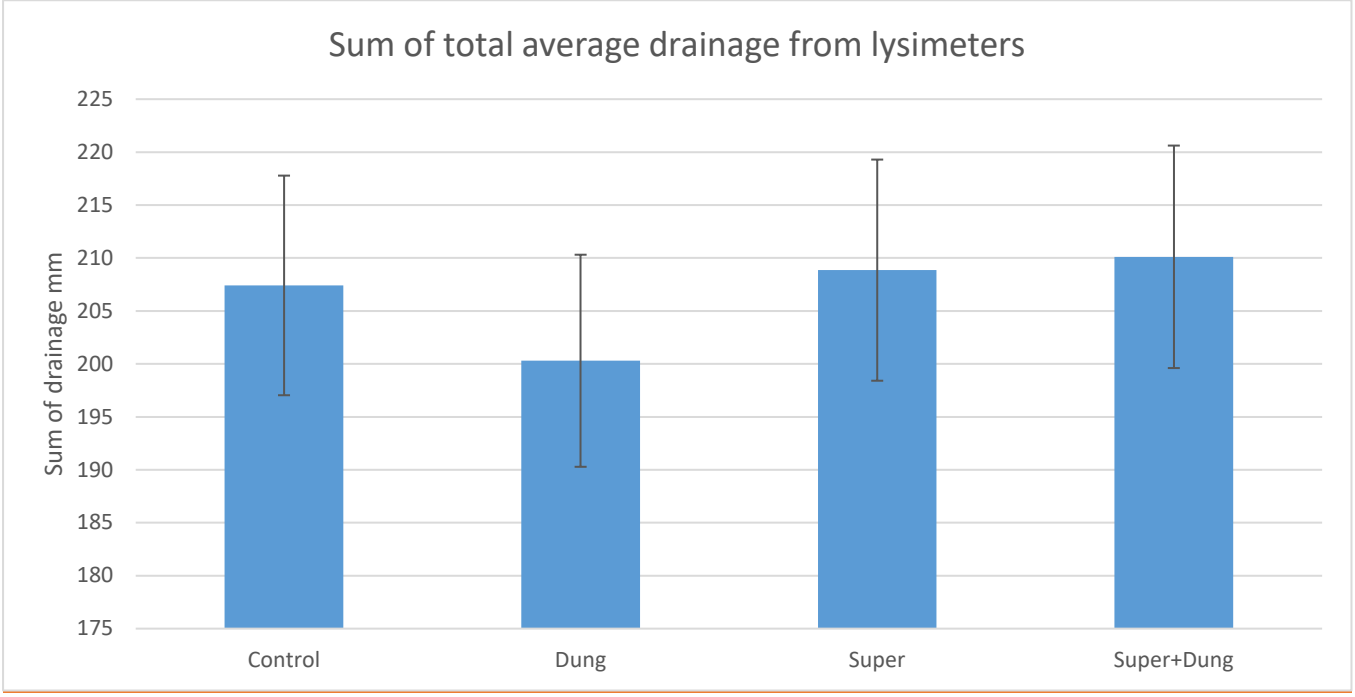


Figure 20: Rainfall for the period of the 29th of October 2015 to end of March 2016.

3.3. Lysimeter trial results.

Results are presented for the lysimeter trial conducted at the Invermay Research Station. Treatments were applied on the 29th of October 2015 and the first collection occurred the following day after irrigation had been applied.



Error bars at the 95% confidence level.

Figure 21: Sum of drainage recorded from sample collection during the trial period. Based on volume collected and lysimeter surface area.

Across all treatments there was variability of drainage characteristics of individual lysimeters. Lysimeter number 46 of the dung only treatment consistently recorded lower volumes due to clogging of the drainage outlet. Number 2 lysimeter of the dung treatment was also excluded from the results due to problems with edge flow. Both were excluded from the results.

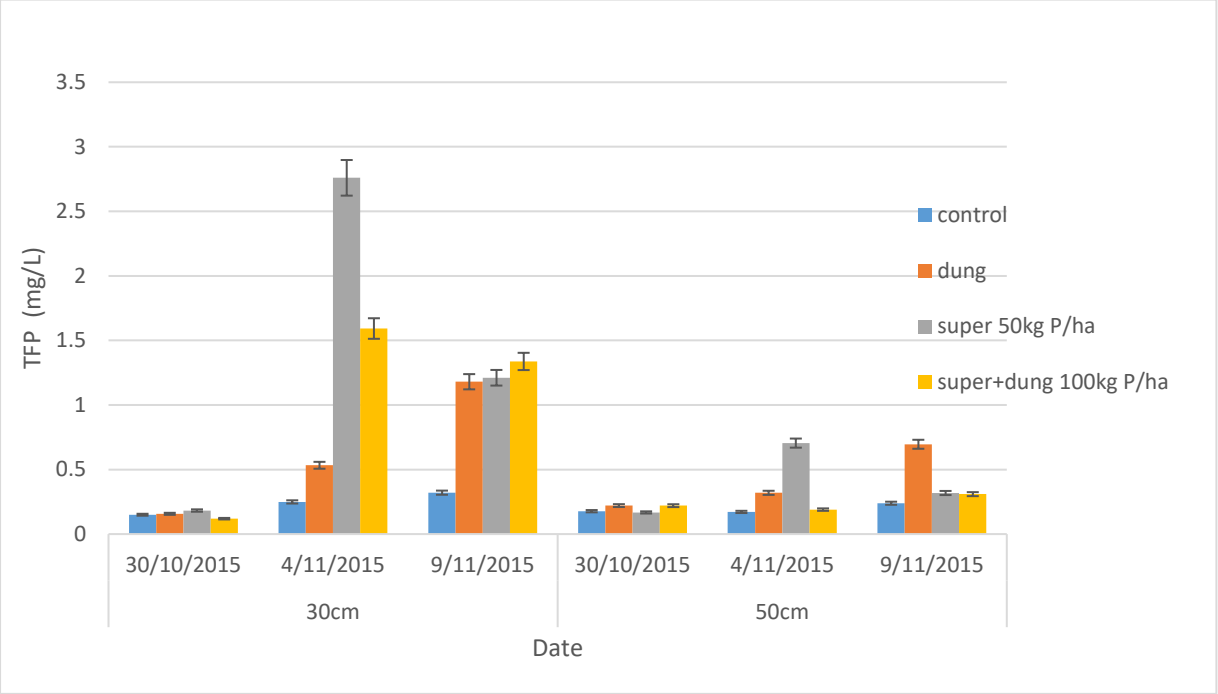
Analysis of variance indicated that P fractions within the lysimeters were not significantly different before application, however the first sampling after treatments were applied shows a significant difference in FRP, TFP and TP between the control and all other treatments ($P < 0.05$).

Table 3.3a: The first drainage events after application which saw a marked increase in FRP, TFP and TP from all treatments excluding the control, however only the Super 50kg/ha treatment was shown to be statistically different at the 30cm depth during the first week after treatments were applied.

	FRP (mg/L)	**TFP (mg/L)**	**TP (mg/L)**
control			
30cm			
30/10/2015	0.088 (0.04)	0.149 (0.02)	0.234 (0.03)
4/11/2015	0.147 (0.06)	0.249 (0.03)	0.307 (0.05)
50cm			
30/10/2015	0.060 (0.02)	0.177 (0.01)	0.369 (0.17)
4/11/2015	0.044 (0.01)	0.171 (0.01)	0.530 (0.17)
dung			
30cm			
30/10/2015	0.177 (0.09)	0.156 (0.03)	0.340 (0.12)
4/11/2015	0.414 (0.16)	0.533 (0.06)	1.336 (0.14)
50cm			
30/10/2015	0.053 (0.01)	0.220 (0.02)	0.542 (0.26)
4/11/2015	0.329 (0.14)	0.319 (0.07)	0.832 (0.29)
Super 50kg P/ha			
30cm			
30/10/2015	0.066 (0.01)	0.182 (0.04)	0.276 (0.07)
4/11/2015	0.603 (0.11)	2.759 (0.48)	3.546 (0.68)
50cm			
30/10/2015	0.043 (0.006)	0.167 (0.02)	0.604 (0.28)
4/11/2015	0.543 (0.25)	0.704 (0.32)	0.880 (0.40)
Super+dung 100 kg P/ha			
30cm			
30/10/2015	0.051 (0.01)	0.119 (0.005)	0.276 (0.06)
4/11/2015	0.450 (0.09)	1.592 (0.33)	2.510 (0.48)
50cm			
30/10/2015	0.041 (0.003)	0.220 (0.03)	0.566 (0.38)
4/11/2015	0.073 (0.03)	0.189 (0.02)	0.353 (0.10)

Brackets denote the SE of the Mean.

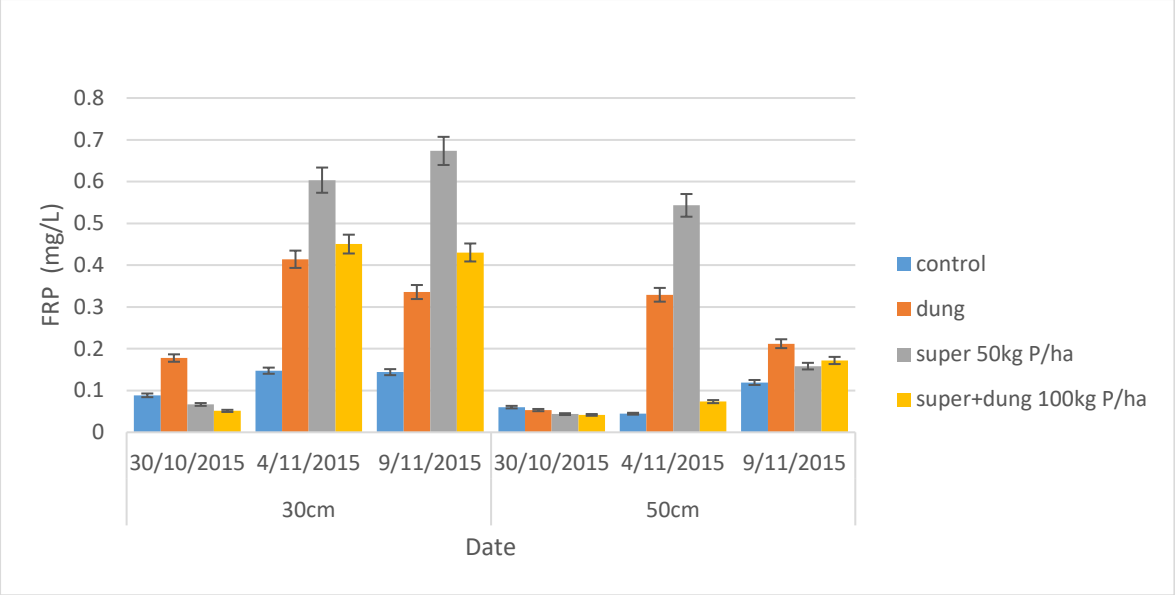
The Super only treatment had the largest loss of FRP, TFP and TP for 2 weeks following treatment application (Figures 22-24).



Error bars at the 95% confidence level.

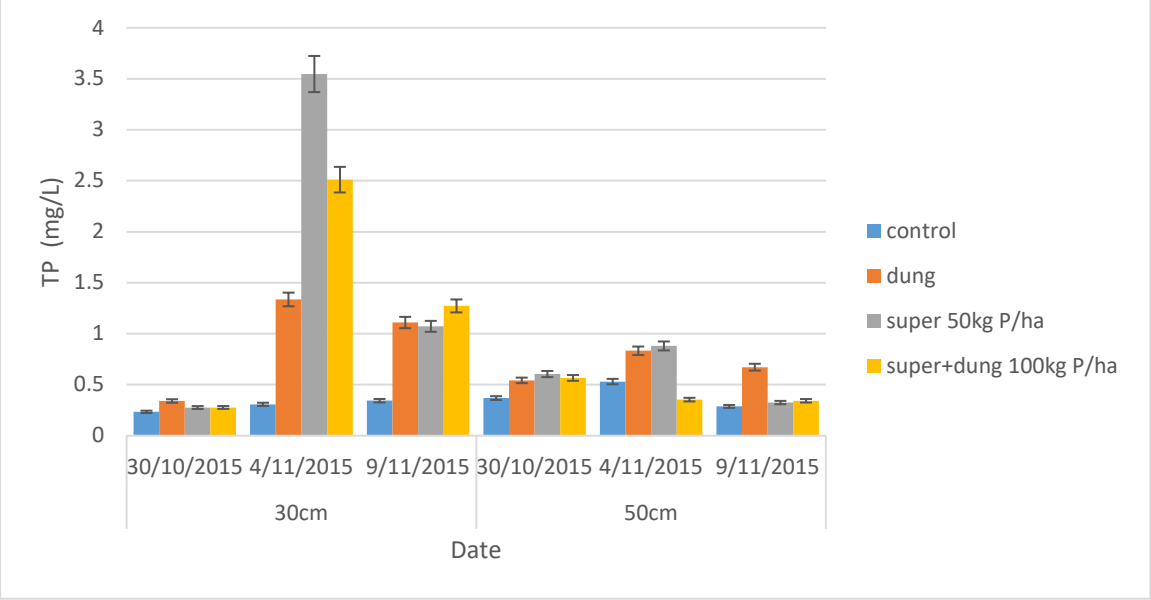
Figure 22: The Super only treatment had the largest loss of TFP during the first week after treatment application, with an average of 2.759 mg/L TFP lost at the 30cm depth and 0.704 mg/L lost at 50cm, compared to 0.249mg/l and 0.171 mg/l for the control treatment.

With a greater proportion of TFP loss in the 30cm depth and decreasing to the 50cm depth. This loss was significantly ($P<0.05$) different between depths for the first 2 samplings after which it then rapidly dropped off to non-significant levels compared with the control.



Error bars at the 95% confidence level.

Figure 23: The Super only treatment had the largest loss of FRP during the first week following treatment application, with an average of 0.603 mg/l FRP lost at the 30cm depth and 0.543 mg/l lost at 50cm.



Error bars at the 95% confidence level.

Figure 24: The Super only treatment had the largest loss of TP within the first week following treatment application, with an average of 3.546 mg/l TP lost at the 30cm depth and 0.880 mg/l lost at 50cm, with the largest loss being from the 30cm depth.

Loads of P fractions measured are presented in Table 3.3b. Results are presented in grams/lysimeter due to only 6 months data being collected from the lysimeters. Results when expressed as $kg^{-1}ha^{-1}yr$ are consistent with findings of (McDowell, 2008, Toor et al, 2004 amongst others) for measured annual TP loss from pastured fields and catchments from dairy systems in New Zealand, at 0.34 to 0.90$kg^{-1}ha^{-1}yr$.

Table 3.3b: Loads of P lost by fraction are presented in grams/lysimeter due to only 6 months data being collected from the lysimeters, therefore not reflecting the true $Kg^{-1}ha^{-1}yr$ value.

Treatment	FRP (g)	FURP (g)	TFP (g)	PP (g)	TP (g)
Control (total)	**0.0133**	**0.0108**	**0.0241**	**0.0223**	**0.0464**
30cm	0.0082	0.0068	0.0150	0.0092	0.0242
50cm	0.0051	0.0040	0.0091	0.0131	0.0222
Dung (total)	**0.0262**	**0.0172**	**0.0549**	**0.0538**	**0.108**
30cm	0.0194	0.0129	0.0323	0.0266	0.0588
50cm	0.0068	0.0043	0.0226	0.0272	0.0498
Super 50kg P/ha (total)	**0.0326**	**0.0180**	**0.0505**	**0.0232**	**0.0738**
30cm	0.0227	0.0136	0.0363	0.0136	0.0499
50cm	0.0099	0.0044	0.0143	0.0096	0.0239
Super+Dung 100 kg P/ha (total)	**0.0290**	**0.0266**	**0.0555**	**0.0326**	**0.0882**
30cm	0.0212	0.0211	0.0423	0.0218	0.0641
50cm	0.0077	0.0055	0.0132	0.0108	0.0241

ANOVA of the means of the overall loads of P lost during the 6 months of the trial, indicate that the control treatment was significantly ($P<0.05$) different to all other treatments with the lowest recorded loss of all P fractions.

Dung and Super only treatments were not significantly different from each other, however the Super + Dung treatment showed the highest overall loss of filterable unreactive Phosphorus (FURP) and was significantly different to all other treatments.
The Super + Dung treatment had the highest loss of TFP, and was significantly different between those treatments that received Dung and Super only.

During rainfall events in November 2015 and January 2016, particulate P (PP) concetrations in the Dung and Dung + Super treatments were significantly different to all other treatments, however when examining the total load of PP it was found that the Dung only treatment was significantly different to all other treatments.
The control treatment was significantly different to all other treatments, with the lowest loss of PP.

Leaching loss data for treatments are given in the Appendix.

Table 3.3c: Pasture cuts were taken from the lysimeter plots in January 2016 and analysed for Total P. Regular pasture cuts were not taken throughout the trial and the results comprise of the first cut after treatment application, and encompass the period of high post application loss of treatment P.

Treatment	Sum of Total P (g/lysimeter).	Average of % P per 100g
Control	0.089 (0.048)	0.27
Dung	0.281 (0.008)	0.33
Super 50kg P/ha	0.098 (0.009)	0.30
Super+Dung 100 kg P/ha	0.270 (0.027)	0.30

Brackets denote the SE of the Mean.

3.4. Mass balance table.

Table 3.4a: Balance of Total P in g/lysimeter. A mass balance takes into account known inputs of fertilizer and compares against outputs of Total P in leachate to the 50cm depth, to account for potential loss below the plough layer of the pasture.

P Inputs	Depth cm	Control	Dung[c]	Super	Super + Dung
Fertilizer		0	0	3.88	3.88
Soil at start	30	16.890	16.890	16.890	16.890
	50	8.243	8.243	8.243	8.243
Dung		0	2.6	0	2.6
P outputs					
Plant[a]		0.290	0.913	0.319	0.877
Leaching	30	0.024 (0.0004)	0.058 (0.0013)	0.049 (0.0016)	0.064 (0.0019)
	50	0.022 (0.0007)	0.049 (0.0014)	0.023 (0.0005)	0.024 (0.0009)
Soil at end[b]	30	15.895 (0.013)	16.499 (0.027)	17.913 (0.190)	17.222 (0.088)
	50	10.439 (0.026)	8.574 (0.042)	11.033 (0.048)	9.012 (0.043)
Unknown loss/gain[c]	30	-0.681	-2.020	-2.489	-5.207
	50	2.508	-1.307	-0.748	-4.810

Brackets denote the SE of Mean.

[a] Plant uptake estimated from P measured in first cut and projected for 6 months.

[b] Soil sampled 12 months after trial start.

[c] Loss does not account for P sequestered in remaining dung pad.

After 6 months there was still visual evidence of dung pads remaining and increased biological activity under the remaining pads. The dung only treatment was still statistically different compared to the control after 6 months.

3.5 Column trial results.

Results are presented for the laboratory column trial conducted at the Invermay Research Station. This laboratory trial was conducted using gravels excavated from below 1m depth at the Omakau site.

Breakthrough curves (BTC) were established for the P compounds presented in Table 3.5a. Compounds were put through the gravel column one time only due to constraints of time and resources, therefore results reflect an indication of the behaviour of the different compounds and not a more detailed analysis that repeating the column treatments would have provided.

Before the P compounds were applied to the columns, a non-reactive solution of Potassium Bromide (KBr) was injected into a saturated column to determine the time at which a steady flow rate of 1 mg/l would be achieved if samples were taken every 10 min and analysed with an ion selective probe. The resulting time to reach steady flow rate was 130 min, which was indicative of 1 pore volume. This result allowed for the determination of the potential time and quantity of samples that would be generated from the multiple P compounds. Results of the KBr application is presented in Figure 25.

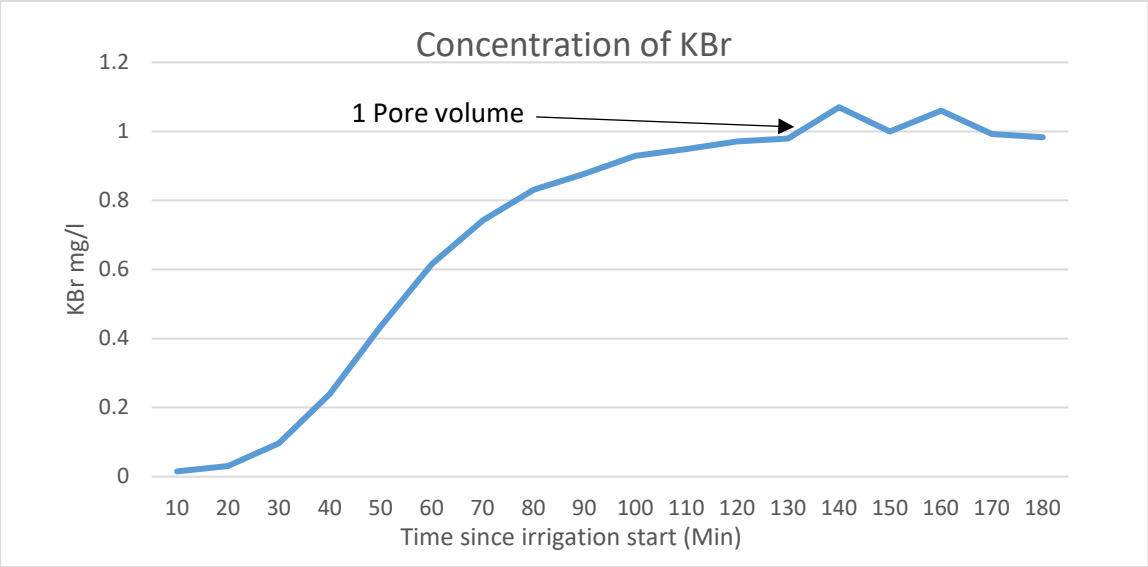


Figure 25: Non-reactive KBr Breakthrough curve.

Results of treatments with and without dung are displayed in tables 3.5a and 3.5b, and give the concentration applied, volume leached, the FRP and TP in mg/L that the treatment reached and the time to reach a steady flow rate. A nonlinear regression analysis was conducted using Genstat 18th edition to examine the relationship between treatments to make statistical assumptions on the influence of the different P compounds. There was no significant difference between the organic P and phosphonate compounds without dung, but there was a significant difference between the inorganic (Potassium dihydrogen) and organic forms of P with dung. Analysis of variance indicated that there was a significant difference in the size of the response from those treatments receiving dung.

Table 3.5a: Column treatments with dung, concentration and time to reach steady flow.

Treatment	Volume ml	Treatment mg/l	FRP mg/l	min	TP mg/l	min
4-nitrophenyl	1200	2	1.04	300	1.63	300
Adenosine	1200	2	0.69	280	0.86	300
Bis p-Nitrophenyl phosphate	1200	2	0.43	220	2.17	140
D-glucose 1-phosphate	1200	2	0.77	260	1.93	160
D-glucose 6 phosphate	1200	2	0.79	300	1.27	300
Guanosine-Monophosphate	1200	2	0.71	280	0.84	260
Lecithin	1200	2	0.43	300	1.06	300
n-(phosphonomethly)glycine 9	1200	2	0.63	280	2.17	280
o-phospho-6-serine	1200	2	1.58	240	2.84	140
phosphocreatine	1200	2	1.25	240	1.96	180
Phytic Acid	1200	2	0.47	280	1.17	220
Potassium dihydrogen	1200	2	2.22	280	2.32	200
Dung	1200	1	0.39	340	1.15	280
Dung+KBr	1200	1	0.30	320	1.05	260

Table 3.5b: Colum treatments without dung, concentration and time to reach steady flow.

Treatment	Volume ml	Treatment mg/l	FRP mg/l	min	TP mg/l	min
4-nitrophenyl	1200	2	0.57	300	1.18	300
Adenosine	1200	2	1.54	260	1.58	200
Bis p-Nitrophenyl phosphate	1200	2	0.87	180	2.0	280
D-glucose 1-phosphate	1200	2	0.52	40	1.12	140
D-glucose 6 phosphate	1200	2	0.44	60	0.89	320
Guanosine-Monophosphate	1200	2	1.54	240	1.82	180
Lecithin	1200	2	0.44	320	1.75	320
n-(phosphonomethly)glycine 9	1200	2	0.94	60	2.05	180
o-phospho-6-serine	1200	2	0.75	240	1.65	200
phosphocreatine	1200	2	0.89	140	1.60	240
Phytic Acid	1200	2	0.86	180	1.28	180
Potassium dihydrogen	1200	2	0.88	300	1.29	320

Although there was a variance observed in the breakthrough times observed within the different organic P treatments, the overall statistical power of the analysis was low and the results highly variable. Fitted curves for FRP for Adenosine and Bis p-Nitrophenyl phosphate without dung could not be fitted to the curve as the asymptote was reversed.

Figures 26 to 30, demonstrate a selection of the BTC's for TP and FRP obtained for the column treatments. A number of BTC's could not be well established, due to a plateau not being reached, so a breakthrough could not be ascertained. Therefore the meaningful BTC's that could be obtained from the column trial are deliberated in the discussion chapter.

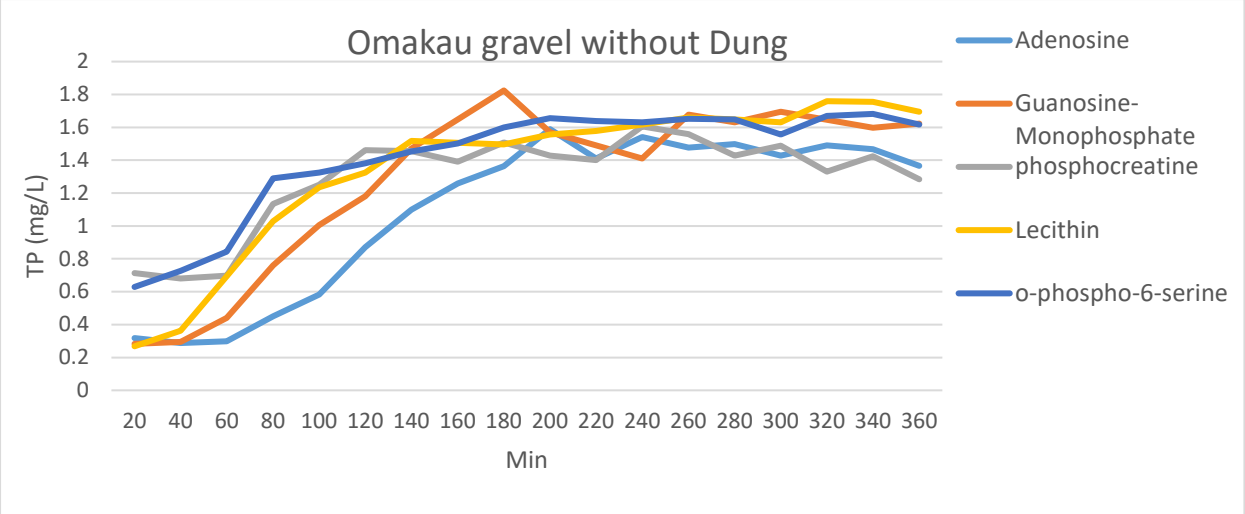


Figure 26: Breakthrough curves of Organic P compounds with dung applied. The initial response from the organic P treatments is similar in response time and attenuation, with treatments of Phosphocreatine and Lecithin showing similar breakthrough times compared with KBr.

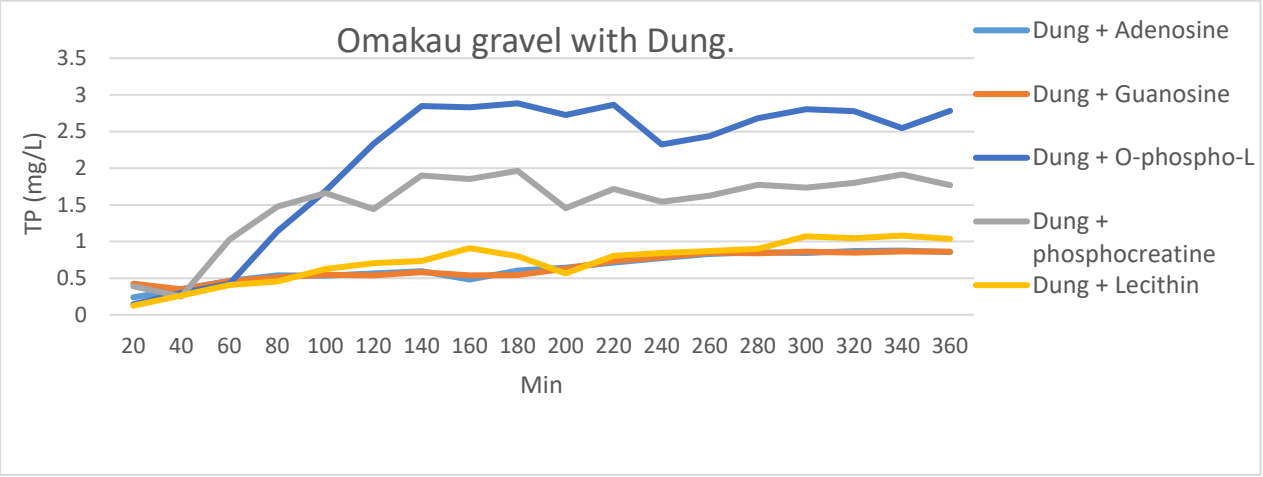


Figure 27: BTC's of Organic P compounds without dung applied.

Figure 27 shows the response of the same Organic P compounds as in Figure 27, with the addition of dung. Phosphocreatine and O-phospho-6-serine show little attenuation when coupled with Dung. With O-phospho-6-serine actually showing an enhanced response. However Guanosine-Monophosphate, Adenosine and Lecithin show a retardation of the breakthrough times and size of the response, with the majority of TP lost comprised of FRP.

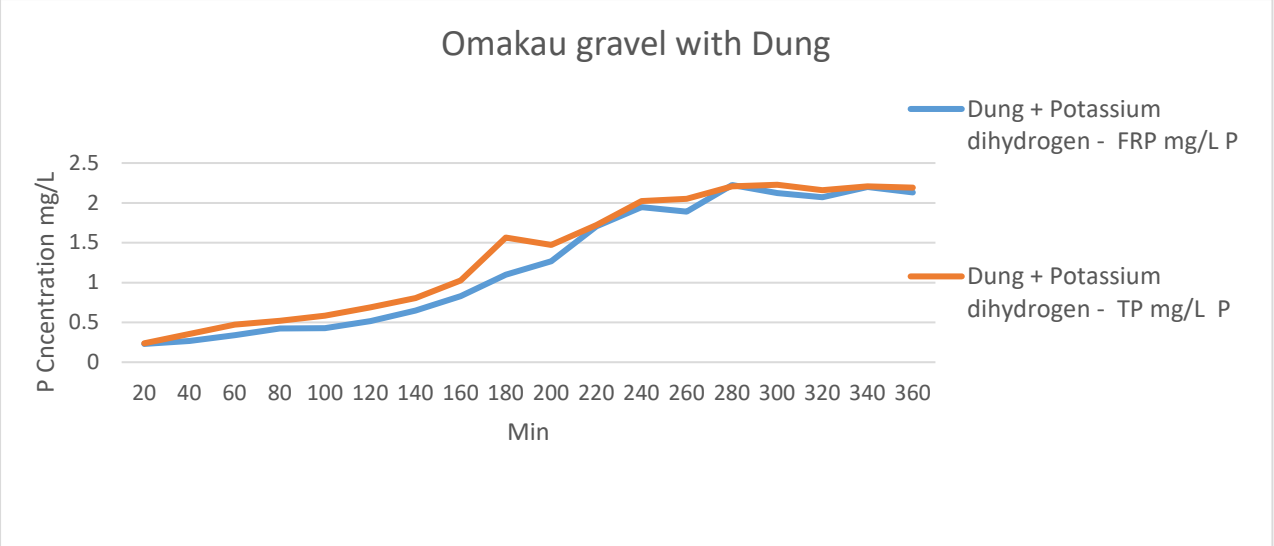


Figure 28: BTC for Potassium dihydrogen with dung. The response to Potassium dihydrogen with Dung, the time to reach a relative steady state is delayed compared to KBr, and that the majority of response is in the form of FRP with 2.2 mg/l FRP within 2.3 mg/l TP. Indicating little attenuation and that P movement is mostly in the dissolved reactive form.

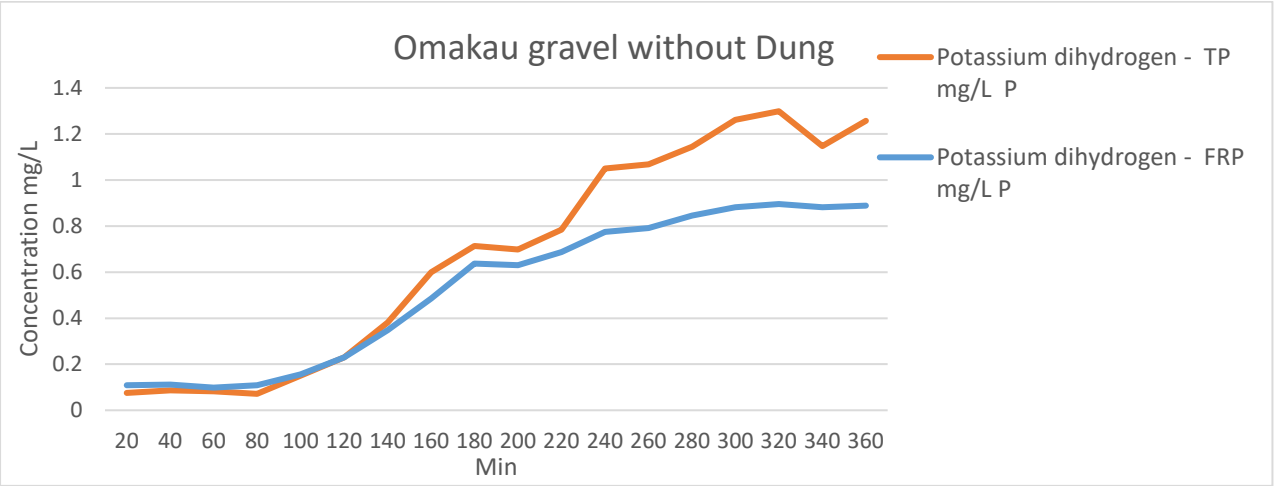


Figure 29: BTC for Potassium dihydrogen without dung. The response of the same inorganic P compound of Potassium dihydrogen, without the presence of Dung. The majority of response is again in the form of FRP with 0.88 mg/l FRP within 1.29 mg/l TP detected, however the size of the response indicates that there is some attenuation of the Potassium dihydrogen occurring within the column.

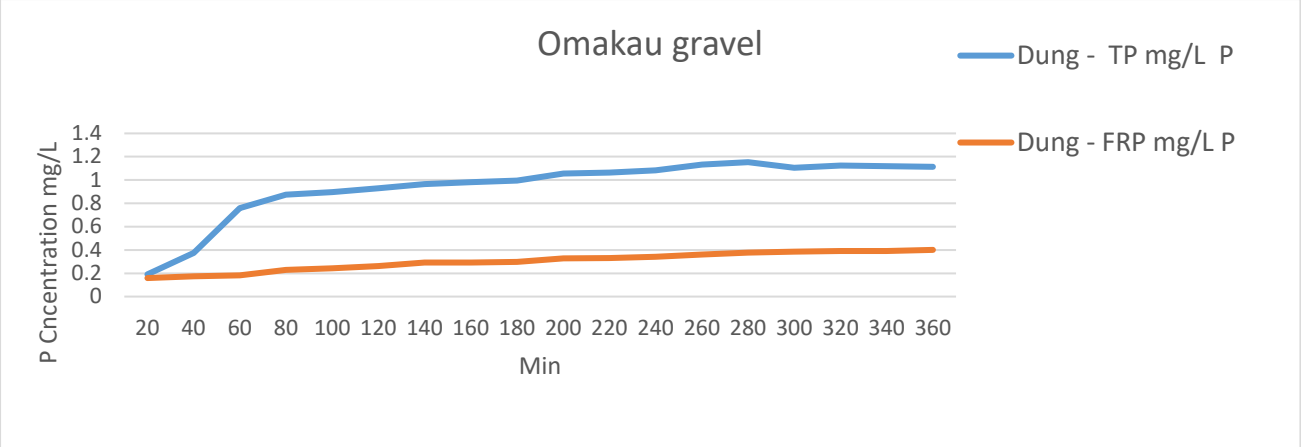


Figure 30: BTC for dung leachate treatment. Dung leachate by its self was shown to have little attenuation within the columns, with 0.39 mg/l FRP and TP of 1.15 mg/l. A large proportion of leachate P from the dung is in the dissolved unreactive form.

3.6. NaOH-EDTA extraction and ^{31} P nuclear magnetic resonance spectroscopy (^{31} P NMR).

A dung leachate concentration of 4.28 mg/L was determined prior to freeze drying of a 5L sample. Extraction of the resulting 2.2g of dried leachate in 40ml NaOH-EDTA yielded a concentration of 2.48 mg/l TP, indicating that close to 50% recovery of P from the leachate sample. After NaOH-EDTA extraction and prior to ^{31} P NMR analysis, Total P and organic P were determined by the difference from orthophosphate before digestion. Results indicate that organic P made up approximately 90% of Total P in the sample. FRP being 0.28 mg/l compared to 2.478 mg/l for Total P (Table 3.6a). ^{31} P NMR was then used to gain a better understanding of the composition and proportions of P classes and compounds within the dung leachate.

Table 3.6a: 0.1M NaOH + 0.05M Na-EDTA extraction results.

0.1M NaOH + 0.05M Na-EDTA	**FRP volume ml**	**FRP (mg P/L)**	**TP volume ml**	**TP conc (mg P/L)**
	0.5	0.28	0.5	2.48

After McDowell and Stuart (2005), peak assignment for ^{31} P NMR were derived from the literature and attributed to between 6.6 and 6.5ppm for Orthophosphate (Newman and Tate, 1980), between 3 and 6 ppm for Orthophosphate monoesters and between -0.5 to 1.5 for Orthophosphate diesters (Markarov et al. 2002).

Results of ^{31} P NMR indicated that there was a sizeable potential pool of Organic P contained in the leachate. Looking at the spectra, only 3 species can be determined (Orthophosphate, Orthophosphate monoesters and Orthophosphate diesters) with the monoesters having the largest proportion.

The ^{31} P NMR spectra shows that orthophosphate is in the minority with an integral of 1.07 compared to monoesters and diesters at 3.27 and 3.09 respectively (Figure 31). This would indicate an Orthophosphate monoester and Orthophosphate diester rounded percentage of 45% each and Inorganic P of 10%. This is consistent with the results obtained from the Lysimeter trial, with FRP accounting for less than 20% of TP load lost from the dung treatment.

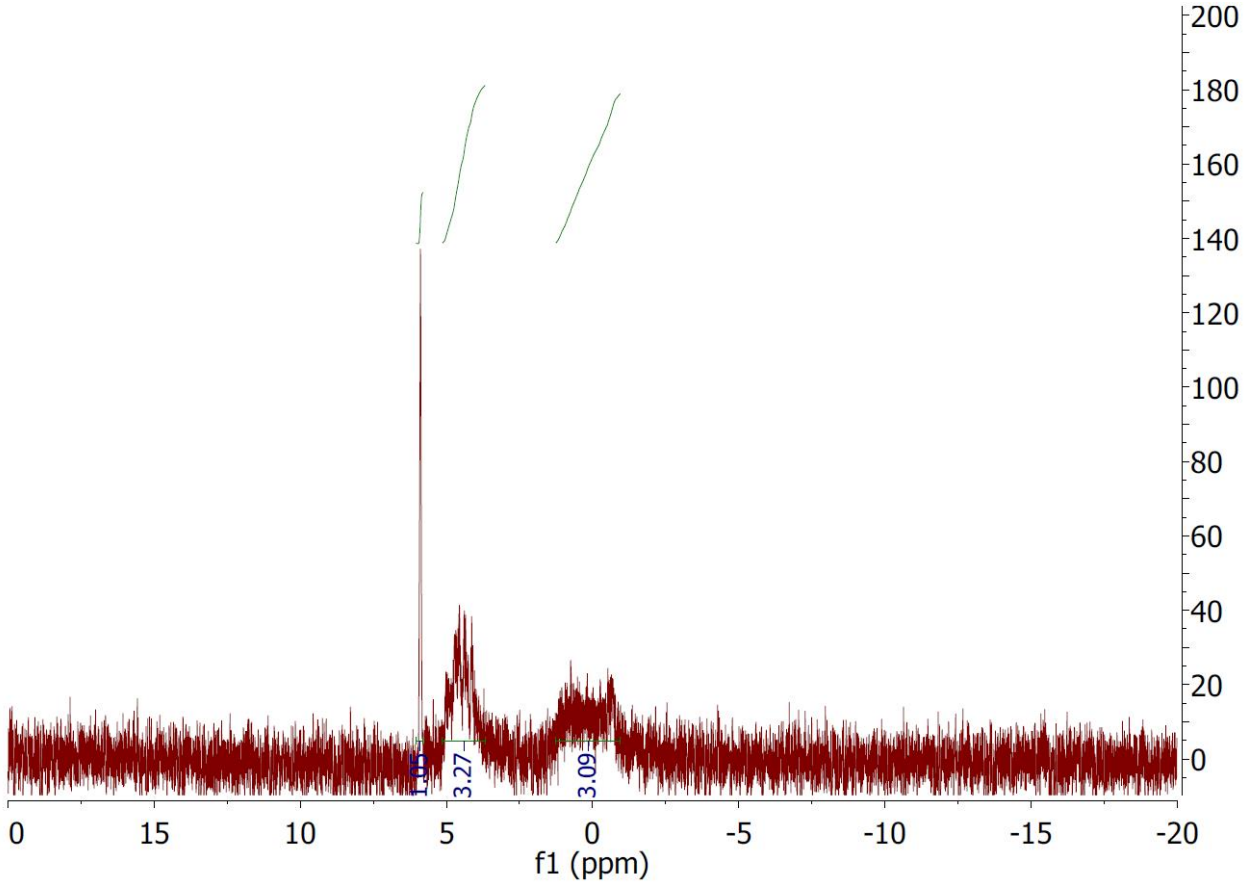


Figure 31: Results of NMR analysis of dung leachate sample.

3.7. Otago Regional Council Lysimeter data.

The Otago regional Council (ORC) maintained a lysimeter at the trial excavation site for a number of years, this allowed for the results of the Invermay lysimeter trial to be compared with data obtained by the ORC.

FRP and TP results for the ORC trial are given in Appendix 3 and give average FRP and TP concentrations and loads at a 1m depth. The appendix also contains trial site information regarding grazing and irrigation times.

Data for TP and FRP concentration and rainfall are displayed in Figure 32 for the groundwater bore site located at Manuherikia, Omakau. Figures 33 and 34 below, give the recorded TP and FRP results as recorded by the ORC.

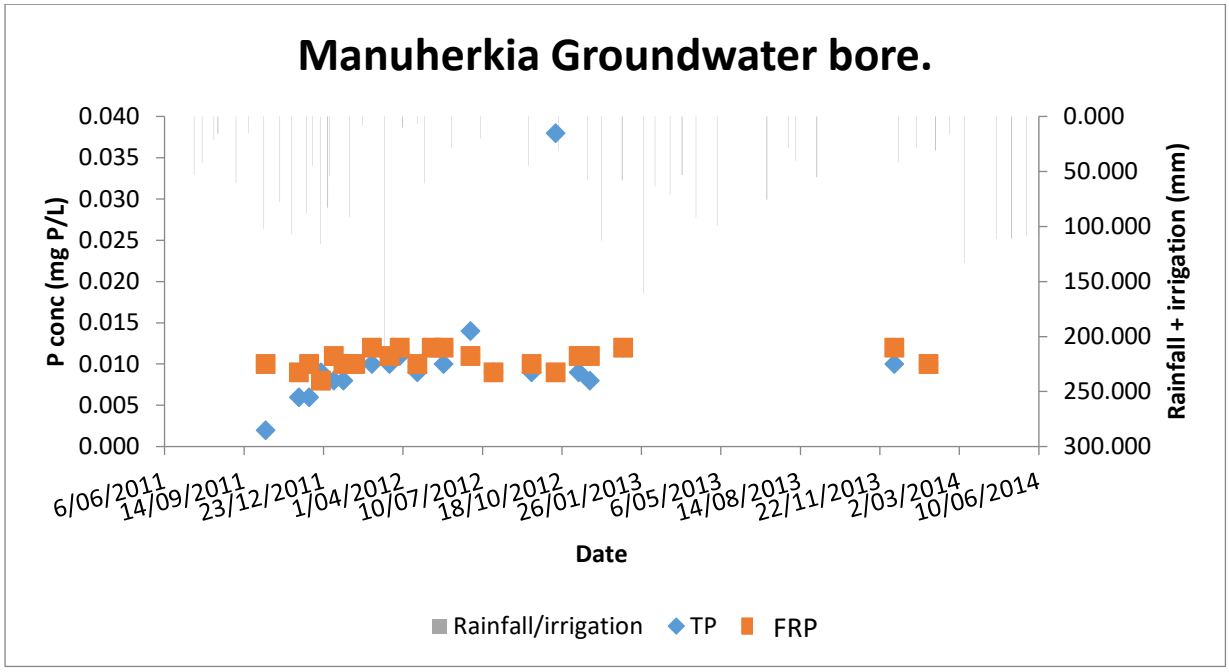


Figure 32: Groundwater bore site located at Manuherikia TP and FRP (ORC 2014).

Figure 33 below, displays the data for the South-arm of the ORC lysimeter. For the periods of September to December 2012 and for periods in mid-2012 to early 2013, no FRP or TP data was recorded.

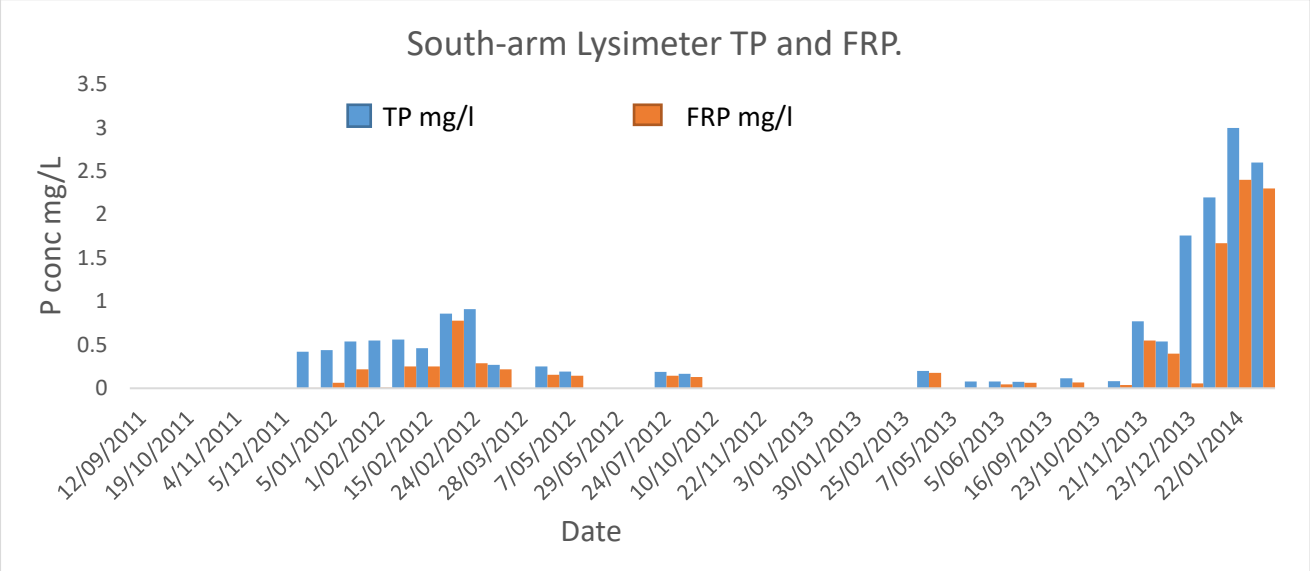


Figure 33: ORC lysimeter South-arm TP and FRP.

Figure 33 below, displays the data for the East-arm of the ORC lysimeter. For the periods of October to November 2011 and May to October 2013, no FRP or TP data was recorded.

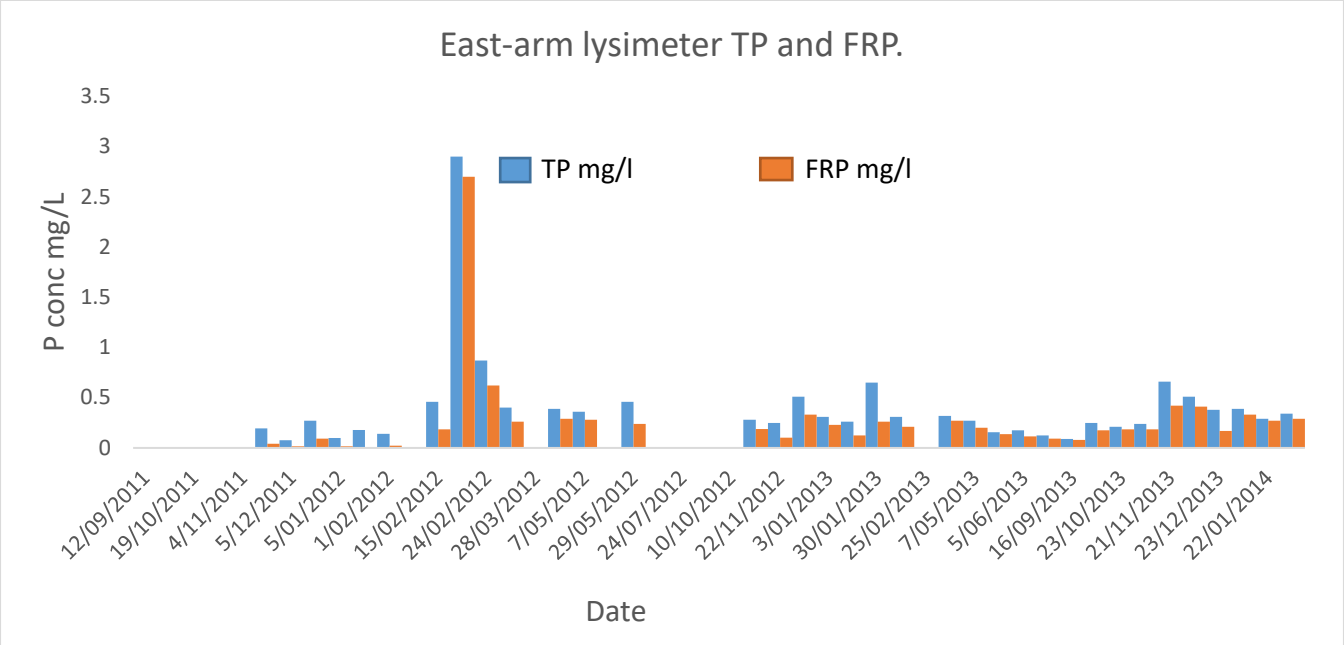


Figure 34: ORC lysimeter East-arm TP and FRP.

Table 3.7a: Summary of anticipated P loss from studied sources.

Site	**Median FRP mg/l**
Leachate to 30-cm	0.115 – 0.321
Leachate to 50-cm	0.067 – 0.213
Leachate to 100-cm. ORC site	0.273
Groundwater	0.010
Manuherikia river	0.018

Table 3.7a gives the median values of FRP lost from the field experiments and data obtained from current ORC and State of the Environment (SOE) reporting.

Data obtained from the ORC deep pan lysimeter was used to compare and inform the hypothesis in conjunction with results from monolithic lysimeters trial and column experiments conducted at Invermay Research Farm and is explored further in the discussion chapter.

Chapter Four: Discussion.

The results of the Lysimeter and column trials will be discussed and the data compared to findings of Otago Regional Council. These findings will then be used in conjunction with wider data describing the hydrological, geological and regulatory environment of the area, to better address the research questions. Conclusions and recommendations for further extension of this work will then be discussed.

4.1 Lysimeter Trial.

This trial was undertaken to address the first research question of vertical P loss, thereby quantifying the forms and mechanisms of P loss, to better inform as to the availability of Organic P and its bioavailability in deeper gravel layers. Recent published work has shown that Alluvial gravels are particularly vulnerable to leaching as they are highly permeable and have sufficient preferential flow paths that allow for rapid transport of P (Carrick et al. 2013; De Bolle et al. 2013; McDowell et al. 2013; Gray 2015). There is also increasing evidence of elevated P concentrations within sand and gravel aquifers underlying soils used for intensive dairy farming (McDowell et al. 2015).

4.1.1 Pathways of P loss.

Analysis of variance indicated that concentrations of P fractions within the lysimeters were not significantly different before treatment application, however the first sampling after treatments were applied showed a significant difference between the control and all other treatments ($P < 0.05$) within a 48 hour period. This suggested that the sorption capacity of the lysimeters was exceeded or by-passed through macropore flow.

Preferential flow and matrix flow are recognised as the major transport mechanisms that can lead to P leaching in a well-structured soil (McDowell et al. 2002, Djodjic et al. 2004, Klienman et al. 2008). For P to be lost in subsurface flow it must first move downward (defined as leaching) below the soil surface either by matrix flow or be preferential flow in soil cracks, large pores vacated by dead plants or earthworm burrows (McDowell et al. 2001). At the start of the trial there can be seen the probable effect of preferential flow, which is most pronounced in the Super only treatments, resulting in a rapid pulse of

nutrients in the form of mostly FRP exiting the lysimeter as leachate. After the initial flushes from the first couple of events, we can see that the flow has changed to a matrix flow dominated transport of nutrients through the monolith in response to applications of irrigation at a low rate. During rainfall events we see that preferential flow again dominates losses, particularly in the dung amended treatments, which have increased loss of P P and FURP.

4.1.2 Fertilizer treatments.

The first drainage events after application which saw a marked increase in FRP, TFP and TP from all treatments excluding the control, however only the Super 50kg/ha treatment was shown to be statistically different at the 30cm depth during the first week after treatments were applied, demonstrating a rapid downward movement of P.

Research has shown that highly soluble P fertilisers such as superphosphate are prone to high incidental loss if applied prior to a flow event (McDowell et al. 2005), this coupled with the high permeability and low P retention properties of the soil may account for this rapid loss after irrigation was applied on Day 1. This response may indicate a loss of potentially bioavailable P in the form of inorganic polyphosphates that are present do not react with molybdate and are therefore counted in the organic P pool (McLaughlin et al. 2011).

4.1.3 Dung treatment.

Those treatments that received dung are deemed to have contributed the most towards saturation of P sorption sites resulting in the loss of mostly dissolved P. The large localised pool of available P which when combined with other organic constituents within the dung and a low ASC, has led to competition for anion sites and enhanced the downward movement of P.

Animal manure patches have been shown to provide an immediate and long term source of largely water soluble P, which can under the correct conditions can be transported by run-off or leached into soil (Chardon et al. 2007; Lucci et al. 2013). Results of lysimeter treatments that received dung would indicate that these soils have a high potential to leach P contained in dung pats, not just by preferential flow but also over an extended period of

time as indicated by the dung treatments still leaching significantly different amounts of TP compared to other treatments, even after 6 months.

4.1.4 Loss of bioavailable P.

It was observed that the FRP mg/l concentration determined during the leaching events exceeded the ANZECC (2000) trigger values for eutrophication of lowland rivers, this applied to all treatments, including the control.

It should be noted that although significant levels of FRP, beyond the ANZECC (2000) guidelines trigger values were detected in the leachate, the potential for P movement into surface waters via groundwater is dependent on drainage into ground water and the connection between groundwater and surface water. The form in which P enters and reacts with surface water, whether organic, in organic, particulate or dissolved will determine the bioavailability and in stream water quality (McDowell et al 2015).

During rainfall events in November 2015 and January 2016, PP in the Dung and Dung + Super treatments were significantly different ($P<0.05$) to all other treatments. This is presumed to come from higher concentrations of particulate P contained in manures, moving through macro pores during increased drainage events. The control treatment was significantly different to all other treatments, with the lowest loss of PP reflecting the smallest pool of potential Particulate available P.

Results conclude that there is a significant difference between the losses of P between the 30cm and 50cm plots, although there is attenuation occurring within the root zone the low P retention capacity of the soil leads to significant loss downwards towards the vadose zone.

The loss of P in subsurface flow has been shown to decrease as P comes in contact with sorption sites within the soil matrix, this however may not occur where organic matter together with low P-sorption capacity i.e. sandy soils or gravels occur (McDowell, 2012).

We also conclude that the load of P lost reflects the rate of P applied, based on the results of the mass balance examination, which suggests that losses are comparable to the application rate of P, but may be enhanced when applied as dung.

This is feasibly due to the inhibition of P sorption sites by organic compounds in dung. Across all treatments those with a higher potential pool of leachable P were shown to exhibit the most response to irrigation, it is therefore reasonable to assume that with increased available sources of P that the risk of loss to the vadose zone increases under these soil types as preferential flow paths transport potentially bioavailable P to receiving waters.

4.1.5. Soil enrichment to depth in lysimeters.

Results of the post chemistry soil analysis indicate P enrichment was greater in lysimeters treated with Super than Dung and the difference magnified in the Super + Dung treatment. The enrichment of the soil down to the 50cm depth can be observed, and in the case of the control and super only lysimeters, there has been a significant loss of P and a change in measureable Olsen P within the top soil layers.

At the commencement of the trial Olsen P was an average of 25 mg/kg within the top 10cm of soil, there has been sharp decrease to 6 mg/kg P within the control lysimeters. It is presumed that Olsen P has sharply decreased due to the usable pool of inorganic P being lost to pasture production and leaching down the soil profile. There is evidence of increased water soluble P (WEP) and TP concentrations across all treatments and increasing with depth.

Haygarth et al. (1988a) reported that concentrations of Olsen P were typically larger at the surface and decrease with depth under permanent pasture. This change is attributed to changes in the forms of P in different transport pathways, with Inorganic P dominating at the surface with inter and overland flow, but organic forms of P made up to 50% of the P transferred to deep drains 85 cm deep, Haygarth et al. (1998b). McDowell et al. (2001) also described that during transport in subsurface flow P concentrations and forms may change.

Chardon et al. (1997), has also reported the presence of higher proportions of dissolved organic P at depth, with 70% of TP at 70 -80 cm depth, indicating a decrease in the proportion of FRP due to sorption in the upper soil horizons. However the magnitude of Olsen P loss is unexpected over such a short time. It must be surmised that the loss reflects the lithology of the media coupled with the low ASC. Further investigation, beyond this research would enhance understanding of the mechanisms involved.

4.2. Mass balance.

The mass balance has attempted to quantify the losses over the course of the lysimeter trial, and has taken into account known inputs of fertilizer and dung. This then has been compared against outputs of total P in leachate and plant uptake. This enables us to estimate the potential loss of bioavailable P below the plough layer of the pasture.

Results show that all treatments display a downward movement of P and enrichment in the top soil (30cm) and sub soil (50cm) depths. This gain in measurable total P must be interpreted in combination with a decrease of plant available P in the upper soil layers and leaching losses beyond enrichment, as FRP is utilised or lost to leaching and transformation to more reductant forms in the lysimeter.

Dung treatments have the highest plant uptake of P, as opposed to super which has an uptake close to the control treatment. This is presumed to be in response to the rapid leaching events within the first 2 weeks of the trial, which saw the Super treatment lose significant amounts of P in the FRP form compared to other treatments.

Treatments of Dung and Super display increasing loss in response to the size of the available pool of leachable P. The size of the Super + Dung treatment loss is comparable to the Super and Dung only treatments combined. This supports observations made of leaching response to fertilizer and dung treatments.

Not reflected in the mass balance table is the contribution of the ongoing pool of plant available P derived from the manure pads. It was observed that the treatments receiving dung had retained a higher Olsen P in the top 10cm of soil compared to other treatments. This would indicate that the loss observed in the mass balance table is overestimated and does not account for the P sequestered in the pad and soil upper layer.

Caution must be used in interpreting the reported plant uptake data, as this is an estimate only and may not reflect the true plant utilisation.

4.3. Lysimeter summary.

Therefore in summarising the findings of the lysimeter trial, it has been determined that there is an enhanced vertical P loss under this soil type, and that ASC combined with a highly permeable subsoil layer would lead to increased rates of P loss. This loss can contain amounts of bioavailable FRP that exceed trigger values set for stream water quality health. These losses also contain significant levels of organic P that has the potential to become bioavailable through P cycling processes below the subsoil layer. These losses have been shown to alter the in-stream chemistry of receiving surface waters especially when soils are hydrologically connected to unconfined shallow aquifers that feed base flows of rivers during low flow periods.

It should be acknowledged that the use of lysimeters to describe field situations is problematic. The scale at which the lysimeter trial was conducted does not take in to account the spatial variability of the soils in question and results need to be considered within the limits of the lysimeter method. Carrick et al. (2014), reported high variability between individual lysimeters on a young stony soil and attributed this to the presence of a sand lenses contained in the lysimeter extraction trench, this sand lenses resulted in variable lag response times from individual lysimeters and changes to the chemical species of the leachate as residence time of filtering differed. As opposed to a strong preferential flow from the stone dominated subsoil matrix. The location from which the lysimeters were taken will contain remnant stream channels and other geological features that would limit the accuracy of lysimeter work. Losses of P may also be overestimated due to compaction within the lysimeter soil layers from irrigation, which is possibly changing the bulk density of the soil. This would mean that more P is being held in the bottom layers. This would require further analysis beyond this study of the soil layers to determine if this is the case.

4.4 ^{31} P NMR.

Dung leachate used within the lysimeter experiment was analysed to determine the species of P that could be identified. Distinguishing between inorganic and organic P was conducted spectrophotometrically with organic P determined as the difference between inorganic P (pre digestion) and Total P (post digestion). The extraction was conducted using a method originally developed by Bowman and Moir (1993). In this method, the alkaline extractant NaOH solubilizes organic matter and EDTA increases the effectiveness of organic P extraction by breaking down P-containing Al and Fe complexes from soil (Koopmans et al 2007). However the alkaline extraction process has been shown to lead to degradation of the Diester P to monoesters (Tuner et al.2003).

Total P and organic P results after 0.1M NaOH + 0.05M Na-EDTA extraction, indicate that organic P made up 90% of Total P in the sample. FRP being 0.28 mg/l compared to 2.478 mg/l for total P. However, it has been reported that organic P is overestimated by this method as inorganic polyphosphates as well as colloidal P, that are present do not react with molybdate and are there counted in the organic P pool. Organic matter present in solution can also interfere with the spectrometer readings, further increasing errors in measurement (McLaughlin et al. 2011, Ron Vaz et al.1993).

Looking at the results of the ^{31} P NMR spectra, only 3 species could be determined (Orthophosphate, Orthophosphate monoesters and Orthophosphate diesters) with the monoesters having the largest proportion. This shows is that orthophosphate is in the minority with an integral of just over 1 compared to monoesters and diesters at just over 3 each. Indicating that organic P accounted for 90% of the detectable P in the sample of which approximately 45% can be ascribed to each class of orthophosphate monoesters and orthophosphate diesters (Figure 35).

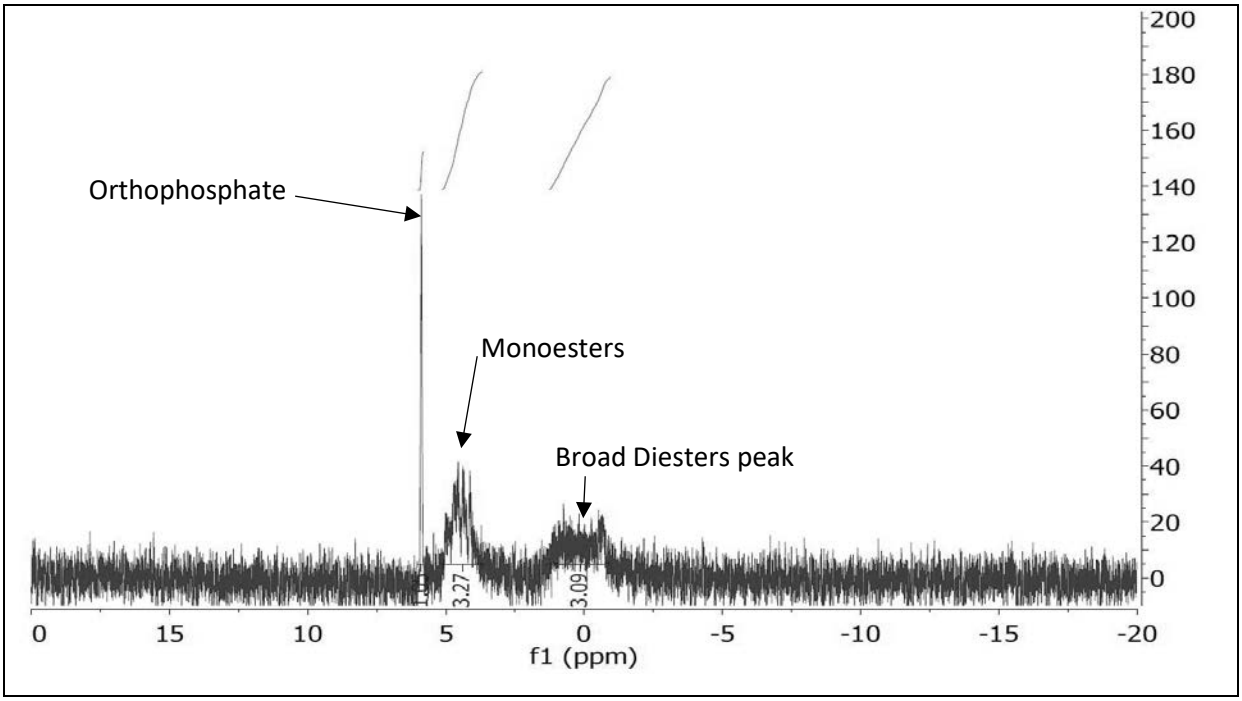


Figure: 35. Species detected in ^{31} P NMR spectra.

There are fewer species detected in the spectra than reported by other studies, absent from the spectra are inorganic compounds of pyrophosphates (-4.3ppm) and polyphosphates (-3,9ppm) and organic compounds of phosphonates (8 to 27.9ppm) (McDowell et al.2007). The absence of these compounds may in part be ascribed to peak broadening due to extraction of high concentrations of paramagnetic ions present in the solution such as Iron (Fe) and Manganese (Mn). These are reported to degrade attainable signal strength Cade-Menun and Liu (2014).

4.4.1: Organic P.

Toor et al. (2003), found in a study of a free draining Lismore silt loam that 89% of leachate P was in the form of organic P and that this organic pool was dominated by orthophosphate monoester P. Other studies have found similar high levels of organic P in manure leachate, (Idowu et al.2008; Koopmans et al.2007; Toor. 2005). Therefore the detected range of organic P from the leachate examined is deemed to be likely representative of the inorganic to organic P ratio.

4.4.2. Orthophosphate monoester P.

Monoesters can include a range of organic compounds (e.g. Nucleotides, inositol phosphates) with peaks that can overlap. In this spectra, the peaks around the monoester range were too small and unresolved to differentiate between specific monoesters.

However, it is seen that monoester P dominates over diester P. The enrichment of Monoesters in this spectra may be attributed to increased inputs from the dung of organic P as inositol phosphate, which may account for up to 80% of organic P in some manure leachate (Turner et al. 2004, Toor et al. 2003 and Toor et al. 2005). Leytem et al. (2002), also reported that monoester P can at times have enhanced sorption over orthophosphate, this can consequently lead to competition for sorption sites and more bioavailable ortho P being lost in solution. Therefore the concentration of monoester P in the sample tested, directly relates to the potential loss of bioavailable P.

4.4.3 Orthophosphate Diester P.

Diesters can include a range of nucleic acids (DNA, RNA), teichoic acids and phospholipids. As with the monoesters, no determination of individual diester compounds could be made. The size of the diester pool detected in the leachate is higher than can be found in many of the reported literature and may be the result of the NaOH-EDTA extraction method.

It has been reported that peaks visible within the diester range are not visible when using differing extraction methods i.e. HCL-NaOH-Clelex (Cade-Menun et al.2014). This may lead to another potential source of variance within the spectra, and may account for an overestimate of diester P.

Diesters P has been shown to be more labile then monoesters within certain soils and can be rapidly hydrolysed for use by plant uptake or lost as soluble P down the soil profile (Leytem et al. 2002). Therefore, this diester pool is representative of a readily hydrolysable source of labile bioavailable P the leaving the subsoil. McDowell et al. (2006) reported up to 35% of TDP measured from field lysimeters in a pasture paddock was Dissolved organic phosphorus (DOP) with the potential for hydrolysis and as such represents a large source of readily bioavailable P.

As it has been shown in the results of the lysimeter and column trials, this pool of Organic P is mobile within the subsoil and deeper gravels and can be enhanced in the presence of

dung, and therefore represents a potential risk to connected surface waters. The next chapter reviews the findings of water quality monitoring within the Alexandra basin area and the risk posed by activities that enrich receiving waters with bioavailable P.

4.5: Column trial experiment.

Describing and predicting P transport behaviour in a porous medium such as gravel is essential to determine if leachate is able to make it into aquifer gravels and re-emerge as stream base flow. The complexity of the physical, chemical and biological interactions within stony soils is an area that requires research in the face of farming intensification in these areas. Such porous media are also naturally heterogeneous and this heterogeneity further complicates the prediction of how different solutes will react.

The column experiment was conducted using a variety of different organic P compounds representative of monoester, diester and orthophosphate which were the most likely P forms in the leachate of the most P enriched treatment (Super+Dung). Column breakthrough curves (BTC) of organic P compounds were examined for species behaviour and compared to orthophosphate (as KH_2PO_4), with or without the presence of dung treatment leachate, as an indication of mobility.

4.5.1. Bromide tracer test.

The use of a bromide tracer at 1mg/l, introduced to the packed columns at the same application rate as the proposed treatments, demonstrated the response of a non-reactive tracer to the gravel media. The generation of a BTC for the tracer verified the minimal attenuation of an inert solute, and also confirmed the absence of preferential flow which may have occurred, if the packing of the columns was inadequate or there was an edge flow effect.

4.5.2. Column treatments.

Treatments were run in groups of 6 columns at a time and samples were taken at regular 10 min intervals over the course of each treatment application, giving 36 data points for each column. This was decided as the maximum that could be acceptable for the analysis for FRP and TP to be completed the same day by colorimetric analysis. In addition to the organic P compounds a KBr treatment was run concurrently during the column runs with an attached solid state Ion selective electrode probe to indicate a relative steady flow state of the solute.

Due to the unknown attenuation of the P compounds in the media, it was decided to use the KBr relative steady flow state as a guide and continue to take samples out to a maximum of 3 hours (approximately 3 pore volumes) to give the best comparison.

4.5.3. Statistical analysis.

A nonlinear regression analysis, followed by an analysis of variance was carried out on the results for the differing P compounds. There was no significant difference determined between the Organic P and phosphonate compounds without dung, but there was a significant difference between KH_2PO_4 and varying organic P compounds with dung leachate. Analysis of variance indicated that there was a significant difference ($P<0.05$), in the size of the response from selective compounds combined with dung leachate.

4.5.4 Column trial summary.

It is important to note that dung leachate by itself was shown to have little attenuation within the columns, and as was reported from the ^{31} P NMR result, a large proportion of leachate P is in the dissolved unreactive form. There was an initial fast spike in TP concentration early on in the dung only column, which may be indicative of edge flow present in this column, however the breakthrough time compared to KBr is still retarded, suggesting an evening out to a more matrix driven flow.

It was found that the KH_2PO_4 treatment receiving dung had a larger response, than without dung. Unexpectedly, the response was largely in the form of FRP, this could reflect competition for sorption sites by organic residues and dissolved organic carbon (DOC) in the leachate, leading to more ortho P being leached or early P saturation of available anion sites within the media, again leading to increased loss. Whereas the KH_2PO_4 only treatment shows retardation in the size of the response, although breakthrough times are similar. This retardation is in response to higher sorption to media surfaces with less competition for sorption sites compared to treatments with dung.

Kang et al. (2011), in a study of manure amended columns found that there was evidence that DOC in manures may decrease P sorption, thereby enhancing P mobility in soils. This enhanced movement was also described as feasibly originating from chemical reactions that controlled adsorption-desorption of P between soil solution and solid phases. The presence

of low weight molecular organic acids, and soluble humic and fulvic acids were also determined to increase the occurrence of enhanced P mobility.

Organic P compounds showed a variety of responses to the addition of dung leachate. Phosphocreatine, Bis-Nitrophenyl and O-phospho-6-serine showed little attenuation and a quicker breakthrough when coupled with dung leachate as opposed to the compounds on their own. This loss was mainly in the form of organic P. However Guanosine-Monophosphate, Adenosine and lecithin show a retardation of the breakthrough times and size of the response, with the majority of TP lost comprised of FRP, when coupled with dung leachate.

This indicates that the dung leachate was the main source attributed to the enhanced P movement/retardation and species absorption-desorption processes within the columns, this diverse response from organic P species would require more exploration beyond the scope of this study to elucidate the answers.

Column trials by their very nature can only be representative of a natural situation, as parameters such as temperature, redox conditions, and flow rate of solutes can only approximate real in-situ conditions. Having such a confined boundary within the column also makes observations of limited reliability, however columns do provide a cost effective means of exploring concepts. The major limitation when conducting this column experiment was the limited number of leaching column replicates that could be conducted. In order to more accurately describe the different compounds, multiple runs of each P compound would be need to improve the statistical power of the trial.

In order to more accurately describe the mechanisms involved in the transport of P into subsurface layers, it would be advantageous to develop a model that incorporates all the components that can be quantified. The model would have to incorporate the hydrological, thermo-mechanical and biological process that control the movement of P.

4.6. Otago Regional Council lysimeter.

In analysing the ORC data, and comparing to the lysimeter trial conducted at Invermay, consistencies in aspects of the results were found. Averaged losses reported across all treatments of the Invermay trial and reported ORC FRP (reported as DRP in ORC data) results are given in Table 4.6a, and propose that losses are occurring to depths that are well above the ANZECC trigger values of 0.010 mg/l.

Table 4.6a: Median FRP (mg/L) for lysimeters.

Site	FRP (mg/L)
Leachate to 30-cm. Invermay.	0.115 – 0.321
Leachate to 50-cm. Invermay.	0.067 – 0.213
Leachate to 100-cm. ORC site	0.273

During the course of the ORC trial, fertiliser application dates and amounts applied were recorded. This allowed for the examination of the effects of pivot irrigation applied effluent in conjunction with super applications. We see a similar response from both trials to the application of fertiliser followed by irrigation on this soil type.

Observations recorded during this period note that from the end of 2011, cow grazing and that pivot irrigation of effluent was applied, we see a sharp rise in TP and FRP that corresponds with the timing of this activity. This demonstrates the response of the soil to increased levels of P and we quickly see enrichment in sub-surface drainage.

450kg p was applied to the paddock containing the ORC lysimeter at the start of 2012. The same day as the fertiliser application, FRP mg/L concentrations spiked to 2.7mg/l after irrigation in the East arm lysimeter. The response seen in the analysed leachate suggests the

presence of macropore flow contributing to rapid leaching to below the vadose zone of this soil.

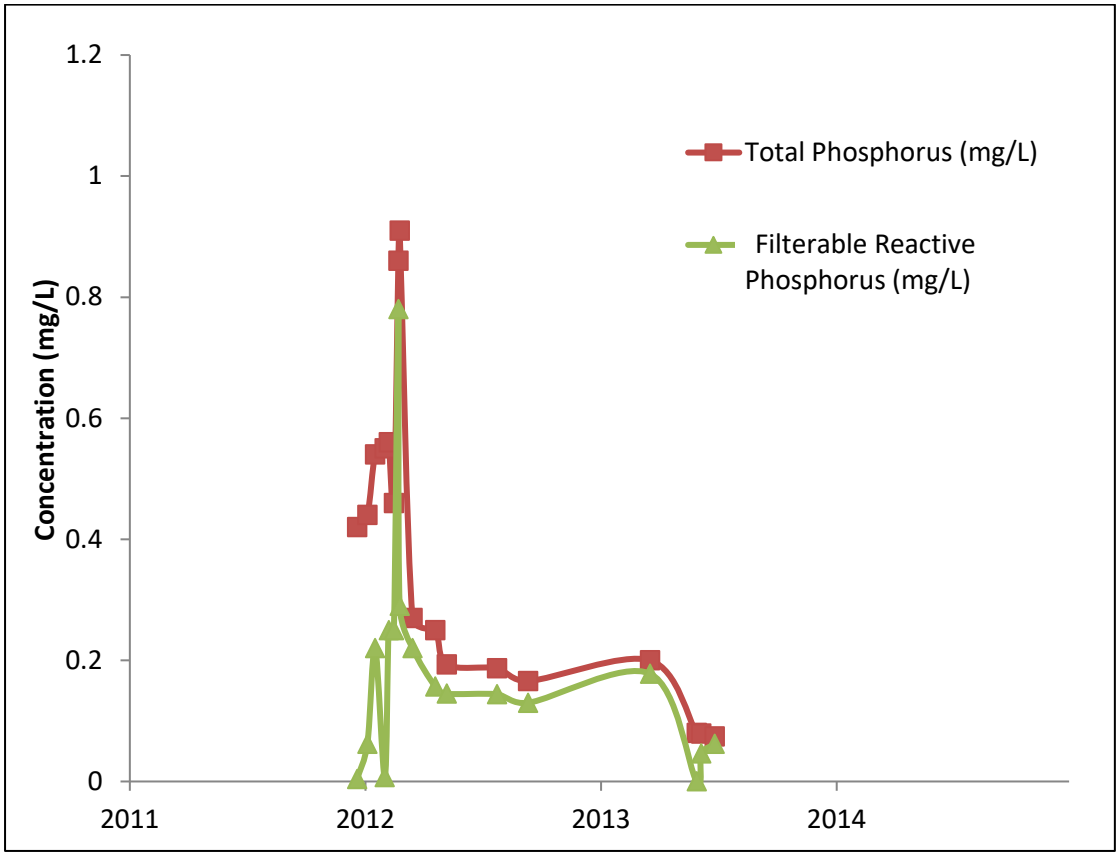


Figure 36: ORC lysimeter Data, TP and FRP. Recorded following irrigation and fertiliser application in the South arm lysimeter. This shows that of the 0.86 mg/l of TP lost during this event that 0.78 mg/l was determined as being FRP.

This would indicate there is the potential for high loss of bioavailable P to deep soil layers and that the loss of P following fertiliser application is dominated by FRP. This also suggests that the attenuation of P in the upper soil layers is being limited by either by-pass flow that limits solute time in contact with soil, or P saturation in the upper layers leading to higher concentration of anions that compete with P for exchange sites.

4.7. Groundwater discharge to Manuherikia River.

In light of the results presented in the experimental work, it is prudent to examine the connection between water leaving the vadose zone through leaching and the potential impact on surface water. The Manuherikia alluvial aquifer has been described as being well connected to the surface water of the Manuherikia River. In 2012, the Otago Regional Council commissioned a report to explore future ground water allocation for the Alexandra basin. This report describe the aquifer as being a small and thin ground water system with a small amount of storage, but nonetheless important for private domestic and stock watering supply. With the main source of land surface recharge being from infiltration of soil-moisture excess from irrigation practices. Figure 37 below, shows the proportions of the various recharge and discharge flows into the aquifer. Without flow measurement of the springs and seepage points within the aquifer, the values shown are approximate, however there is confidence that that the discharging water from the aquifer contributes to the base flow for the Manuherikia River (ORC 2012).

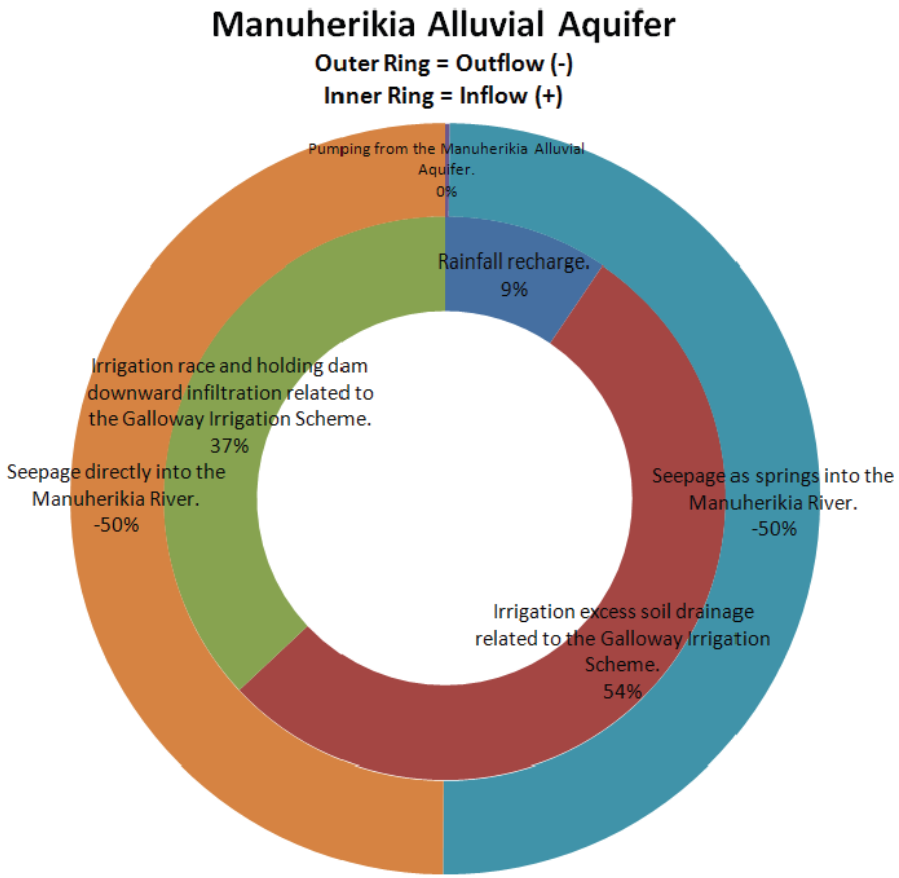


Figure 37: Estimated Maunuherikia water balance, ORC 2012.

The measured values are reported in Table 4.7a and show that the aquifer has a small water balance volume and close associations with the Manuherikia River.

Table 4.7a: Inflow and outflow from the Manuherikia Alluvial Aquifer (ORC 2012).

	Mean annual inflow (Mm^3/y)	Mean annual outflow (Mm^3/y)
Rainfall recharge	0.21	
Irrigation excess soil drainage related to the Galloway Irrigation Scheme	1.20	
Irrigation race and holding dam downward infiltration related to the Galloway Irrigation Scheme	0.83	
Pumping from the Manuherikia alluvial aquifer*		0.00
Seepage as springs into the Manuherikia River		1.10
Seepage directly into the Manuherikia River		1.10
Totals	2.2	2.2
*Note: * Actual pumping estimated as 30% of groundwater take consent allocation for the aquifer*		

It must be noted that although the contribution of the Manuherikia Alluvial Aquifer to the whole basin water balance is modest at 2.2 Mm^3/y compared to the Dunstan, Earnscleugh and Manuherikia Clay bound Aquifer at 10.2, 28.7 and 1.2 Mm^3/y respectfully, the close hydrological connection between Aquifer and River means that activities that influence ground water quality will have an increased chance of impacting surface water quality due to a low residence time of water traveling towards the river.

4.7.1: Surface Water quality of the Manuherikia River

The Otago Regional Council is responsible for managing Otago's surface water resources and carrying out regular long-term water quality monitoring as part of its State of the Environment (SOE) reporting, as well as short term targeted water quality monitoring programmes. Monitoring programmes measure against 5 water quality standards to gauge water quality, being Nitrite-nitrate nitrogen (mg/L), dissolved reactive P (mg/L), Ammoniacal N (mg/L), E-coli (cfu/100ml) and turbidity (NTU). The results of monitoring are compared to the Water quality index (Figure 38) to assign a scorecard rating to the site.

Grade	Number of parameters complying with water quality standards (June 2011 to July 2016)
Excellent	All five parameters (Table 1) comply
Good	Four (of the five) values comply
Fair	Three (of the five) values comply
Poor	Two or fewer (of the five) values comply

Figure 38: Water quality index. Modified from ORC (2012).

In 2011, the ORC conducted an investigation into the water quality of the Manuherikia catchment over the period of 2009 to 2011. The results of which were compared to the 2007 SOE report. The results of the 2007 SOE report indicated the water quality within the catchment was generally 'good' to 'excellent', with no sites having a 'poor' rating. The Manuherikia River is considered N-limited, which is preventing nuisance algal growth, however a change to more intensive farming could potentially occur and the development of new irrigation infrastructure may lead to further intensification, which would put pressure on the water quality and ecological values.

The 2011 report indicates that at the monitoring sites of the Manuherikia main stem, the water quality had decreased. There was a significant increase in TP and FRP at the Ophir and Galloway sites on the Manuherikia and we see a range of classifications from 'excellent' to 'poor'. FRP concentration guideline values were based on Biggs (2000) and set at 0.006 mg/l. It was reported that FRP concentrations were above the guideline value (particularly at low flow) in many of the tributaries of the Manuherikia River, which was most likely from irrigation run-off. This had contributed to increased levels of FRP in the lower Manuherikia River. During the reporting period of this report there had been a change in the varieties of farming activities within the catchment, with an increase in the wintering of dairy herds and the establishment of the first dairy platform near Omakau.

In 2016, the ORC published a report card document for water quality and ecosystem health which reported the sites within the upper and lower Manuherikia River were above the FRP ANZECC (2000) guideline values of 0.010 mg/L, which is to be used as a guideline value under Plan Change 6a. We also see an increase in sites that have a 'poor' rating, which can be reasonably attributed to changes in land use throughout the catchment.

Results of a DeSeasonalised trend analysis, conducted on data obtained from the Land, Air and Water Aotearoa (LAWA) data base indicates that there is a significant trend in increasing FRP concentrations between 2006 and 2016 within the Manuherikia River, with the slope of the trend line fitted to DeSeasonalised data showing an increase of 4.99% per year. Trend analysis is presented in the appendix 3.

When examining the results of the ORC and Invermay Lysimeter trials together, there is evidence of concentrations of FRP beyond the ANZECC (2000) guidelines trigger value of 0.010 mg/l FRP occurring to depth in these stony soil. When viewed in combination with the reported rise in detectable FRP and decreasing stream health in some areas, it can be reasoned that there is a system response from land change and farming practices in this area. Although the results indicate a significant loss occurring, it must be emphasised that this work looked at a sub-section of the entire process and that there are other catchment process that would have an impact on water quality that are beyond the scope of this study to determine.

Chapter Five: Conclusions.

There has been abundant studies conducted on subsurface and groundwater transport of P in recent years (De Bolle et al. 2013; Gray 2015; McDowell et al. 2015)., and it is accepted that P loss to groundwater and subsequent transport to surface waters is no longer an acceptable or negligible loss. There has also been considerable work conducted on the cumulative effects of grazing animals and their effect on nutrient transport. Land use practices must take into account non-point source or diffuse discharge risks relating to subsurface pathways, although this is complicated by the complex interactions between hydrological and chemical processes within the soil matrix.

Results of this body of experimental work show that in respect to the research questions, we determined that there was a significant difference between the losses of P descending downward through the soil profile of an low ASC soil, although there is attenuation occurring within the root zone, the low ASC of the soil leads to substantial loss downwards towards the vadose zone. There is also evidence that the majority of loss occurs in the form of preferential flow.

This loss towards the vadose zone is also enhanced by dung, possibly due to the inhibition of P sorption sites by organic compounds in dung and an increase in the incidence of bioavailable forms of P moving downward towards ground water. As previously stated, the results of the experiments may not represent the true quantitative loss that occurs in the natural system, however when the results are combined with data from the in field deep lysimeter, there is an argument that P is potentially reaching ground water underlying these soils, and could pose a risk to surface water quality.

Currently the receiving waters at Manuherikia River flood plain does not meet FRP limits and targets for achieving good quality water. In the light of proposed changes under Plan Change 6A - OTAGO WATER PLAN, the purpose of which is to manage contaminant discharge and sediment from runoff, drains, leaching and earthworks. Compliance with the future discharge thresholds and will be challenging to meet given the nature of these soils.

There is a need for further research to investigate and model the pathways of P loss in low ASC soils given the extent to which this class of soil is being developed. There is a requirement to increase the understanding of transport times for fertiliser P and effluent P applied to the surface of a low ASC soil to move down the soil profile and potentially into groundwater, particularly in the face of expected dairy growth within the regions. Extending this research by modelling will inform land users as to the potential of P to move into groundwater, in areas where P sorption capacity is poor. This will allow for more informed decision making based on the risk of groundwater-P losses to surface water.

Further research is proposed to examine the Dissolved Organic Phosphorus fractions to determine the amount of bioavailable P that is contributed further to the vadose zone. Solute breakthrough curves can be seen to be an effective method by which to characterise flow pathways and can be applied successfully to high permeability, low ASC soils and future research would benefit from the use of this technique. Understanding the potential for P to move down the vadose zone and into the groundwater in leachate, from common P applications under irrigated and grazed dairy pastures, will enhance the awareness of lowland steam health. However, it is also important that where effects of land uses on water quality are uncertain or unproven, that a precautionary approach is taken by land managers, especially on vulnerable soils.

Acknowledgments

My thanks to my supervisors, Professor Rich McDowell, for the direction behind the thesis and help aiming me in the right direction. Also Professors Jenny Webster-Brown, and Tim Clough for support at the Lincoln campus.

The staff at the Otago University geography department for help with the laser particle size analyser. The Chemistry department of the Otago University for conducting the ^{31}P NMR analysis and Ian Stuart of the chemistry department for providing feedback on the methodology. Many thanks also to the staff and management of AgResearch for the support and encouragement in pursuing this study.

References

Aarons, S. R., C. R. O'Connor, et al. (2004). "Dung decomposition in temperate dairy pastures I. Changes in soil chemical properties." Australian Journal of Soil Research 42(1): 107-114.

Andersson, H., L. Bergström, et al. (2015). "The role of subsoil as a source or sink for phosphorus leaching." Journal of Environmental Quality 44(2): 535-544.

Blake, L., S. Mercik, et al. (2000). "Phosphorus Content in Soil, Uptake by Plants and Balance in Three European Long-Term Field Experiments." Nutrient Cycling in Agroecosystems 56: 263-275.

Bowman, R. A. and J. O. Moir (1993). "Basic EDTA as an extractant for soil organic phosphorus." Soil Science Society of America Journal **57**(6): 1516-1518.

Busman, L., J. Lamb, et al. (2009). "The nature of phosphorus in soils."

Cade-Menun, B. and C. W. Liu (2014). "Solution Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy of Soils from 2005 to 2013: A Review of Sample Preparation and Experimental Parameters." Soil Science Society of America Journal **78**(1): 19-37.

Cameron, K. C., N. P. Smith, et al. (1992). "Lysimeters without Edge Flow: An Improved Design and Sampling Procedure." Soil Science Society of America Journal 56: 1625-1628.

Carpenter, S. R., N. F. Caraco, et al. (1998). "Nonpoint pollution of surface waters with phosphorus and nitrogen." Ecological Applications 8(3): 559-568.

Carrick, S., J.-A. Cavanagh, et al. (2014). "UNDERSTANDING PHOSPHORUS, NITROGEN AND CADMIUM TRANSFER THROUGH A YOUNG STONY SOIL." Nutrient management for the farm, catchment and community. Palmerston North, New Zealand, Fertilizer and Lime Research Centre, Massey University.

Carrick, S., D. Palmer, et al. (2013). "Stony soils are a major challenge for nutrient management under irrigation development." Accurate and efficient use of nutrients on farms.

Chardon, W. J., G. H. Aalderink, et al. (2007). "Phosphorus leaching from cow manure patches on soil columns." J Environ Qual **36**(1): 17-22.

Childers, D. L. (2011). "Response from Childers: Phosphorous challenges beyond the food system." Bioscience 61(8): 582-583.

Condron, L. M. and S. Newman (2011). "Revisiting the fundamentals of phosphorus fractionation of sediments and soils." Journal of Soils and Sediments 11(5): 830-840.

Cordell, D., J. O. Drangert, et al. (2009). "The story of phosphorus: Global food security and food for thought." Global Environmental Change 19(2): 292-305.

De Bolle, S., S. De Neve, et al. (2013). "Rapid redistribution of P to deeper soil layers in P saturated acid sandy soils." Soil Use and Management 29(SUPPL.1): 76-82.

Djodjic, F., K. Börling, et al. (2004). "Phosphorus Leaching in Relation to Soil Type and Soil Phosphorus Content." Journal of Environmental Quality 33(2): 678-684.

Dodds, W. K., W. W. Bouska, et al. (2009). "Eutrophication of U.S. Freshwaters: Analysis of Potential Economic Damages." Environmental Science & Technology 43(1): 12-19.

Dou, Z., C. F. Ramberg, et al. (2009). "Phosphorus speciation and sorption-desorption characteristics in heavily manured soils." Soil Science Society of America Journal 73(1): 93-101.

Dymond, J. R., A. G. Ausseil, et al. (2013). "Nitrate and phosphorus leaching in New Zealand: a national perspective." New Zealand Journal of Agricultural Research 56(1): 49-59.

Edith Allaire, S., E. van Bochove, et al. (2011). "Preferential pathways of phosphorus movement from agricultural land to water bodies in the Canadian Great Lakes basin: A predictive tool." Canadian Journal of Soil Science 91(3): 361-374.

Edmeades, D. C. (2003). "The long-term effects of manures and fertilisers on soil productivity and quality: A review." Nutrient Cycling in Agroecosystems 66(2): 165-180.

Edmeades, D. C., A. K. Metherell, et al. (2006). "Defining the relationships between pasture production and soil P and the development of a dynamic P model for New Zealand pastures: A review of recent developments." New Zealand Journal of Agricultural Research 49(2): 207-222.

Elser, J. and E. Bennett (2011). "Phosphorus cycle: A broken biogeochemical cycle." Nature 478(7367): 29-31.

Gray, C. P., L;Dodd, R. McDowell, R.W; Close, M.E (2015). "Transport of phosphorus in an alluvial gravel aquifer." New Zealand Journal of Agricultural Research 58:4: 490-501.

Hamill, K. D. and G. B. McBride (2003). "River water quality trends and increased dairying in Southland, New Zealand." New Zealand Journal of Marine and Freshwater Research 37(2): 323-332.

Haygarth, P. M., L. Hepworth, et al. (1998). "Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland." European Journal of Soil Science **49**(1): 65-72.

Denison, F. H., P. M. Haygarth, et al. (1998). "The measurement of dissolved phosphorus compounds: Evidence for hydrolysis during storage and implications for analytical definitions in environmental analysis." International Journal of Environmental Analytical Chemistry **69**(2): 111-123.

Haygarth, P.M. & Sharpley, A.N. 2000. Terminology for phosphorus transfer. Journal of Environmental Quality 29: 10-15

Hedley, M. J., R. Hill, et al. (2002). Soil tests and environmental codes of practise. Dairy Farm Management, Palmerston North, Occasional Report No 15. Fertilizer and Lime Research Centre, Massey University.

Holman, I. P., M. J. Whelan, et al. (2008). "Phosphorus in groundwater-an overlooked contributor to eutrophication?" Hydrological Processes 22(26): 5121-5127.

Horta, C. (2015). "Sustainability of phosphorus fertilisation: sources and forms of phosphate." Revista de Ciências Agrárias (Portugal) 38(4): 473-483.

Khan, K. S. and R. G. Joergensen (2009). "Changes in microbial biomass and P fractions in biogenic household waste compost amended with inorganic P fertilizers." Bioresource Technology 100(1): 303-309.

Khan, K. S. and R. G. Joergensen (2012). "Relationships between P fractions and the microbial biomass in soils under different land use management." Geoderma 173–174: 274-281.

Kleinman, P. J. A., A. N. Sharpley, et al. (2011). "Managing agricultural phosphorus for water quality protection: Principles for progress." Plant and Soil 349(1-2): 169-182.

Kleinman, P., A. Sharpley, et al. (2009). "Application of manure to no-till soils: phosphorus losses by sub-surface and surface pathways." Nutrient Cycling in Agroecosystems **84**(3): 215-227.

Koopmans, G. F., W. J. Chardon, et al. (2007). "Phosphorus movement and speciation in a sandy soil profile after long-term animal manure applications." J Environ Qual **36**(1): 305-315.

Kronvang, B., G. H. Rubæk, et al. (2009). "International Phosphorus Workshop: Diffuse phosphorus loss to surface water bodies - Risk assessment, mitigation options, and ecological effects in river basins." Journal of Environmental Quality 38(5): 1924-1929.

Leytem, A. B., R. L. Mikkelsen, et al. (2002). "Sorption of organic phosphorus compounds in Atlantic coastal plain soils." Soil Science 167(10): 652-658.

Longhurst, R. D., A. H. C. Roberts, et al. (2000). "Farm dairy effluent: A review of published data on chemical and physical characteristics in New Zealand." New Zealand Journal of Agricultural Research 43(1): 7-14.

Lucci, G. M., R. W. McDowell, et al. (2013). "Phosphorus source areas in a dairy catchment in Otago, New Zealand." Soil Research 50(2): 145.

Malik, M. A., P. Marschner, et al. (2012). "Addition of organic and inorganic P sources to soil – Effects on P pools and microorganisms." Soil Biology and Biochemistry 49: 106-113.

Makarov, M. I., L. Haumaier, et al. (2002). "Nature of soil organic phosphorus: An assessment of peak assignments in the diester region of 31P NMR spectra." Soil Biology and Biochemistry **34**(10): 1467-1477.

McDowell, R., N. Cox, et al. (2015). "A national assessment of the potential linkage between soil, and surface and groundwater concentrations of phosphorus." Journal of the American Water Resources Association In press.

McDowell, R. W. (2012). "Minimising phosphorus losses from the soil matrix." Current Opinion in Biotechnology 23: 1-6.

McDowell, R. W., B. J. F. Biggs, et al. (2004). "Connecting phosphorus loss from agricultural landscapes to surface water quality." Chemistry and Ecology 20(1): 1-40.

McDowell, R.W. and Condron, L.M. 2004. Estimating phosphorus loss from New Zealand grassland soils. New Zealand Journal of Agricultural Research 47: 137-145

McDowell, R. W. and L. M. Condron (2012). "Phosphorus and the Winchmore trials: review and lessons learnt." New Zealand Journal of Agricultural Research 55(2): 119-132.

McDowell, R. W. and J. A. Kitto (2013). "Assessment, modelling and management of land use and water quality in the upper Taieri River catchment." New Zealand Journal of Agricultural Research 56(4): 261-278.

McDowell, R. W. (2008). "Phosphorus in humped and hollowed soils of the Inchbonnie catchment, West Coast, New Zealand: I. Variation with age and distribution." New Zealand Journal of Agricultural Research **51**(3): 299-306.

McDowell, R. W. (2008). Grazed pastures and surface water quality. New York, Nova Science Publishers.

McDowell, R. W. and G. F. Koopmans (2006). "Assessing the bioavailability of dissolved organic phosphorus in pasture and cultivated soils treated with different rates of nitrogen fertiliser." Soil Biology and Biochemistry **38**(1): 61-70.

McDowell, R. W., R. M. Monaghan, et al. (2005). "Enhanced losses of phosphorus in mole-tile drainage water following short-term applications of dairy effluent to pasture." Water pollution.

McDowell, R. W. and D. Nash (2012). "A review of the cost-effectiveness and suitability of mitigation strategies to prevent phosphorus loss from dairy farms in New Zealand and Australia." J Environ Qual 41(3): 680-693.

McDowell, R. W., A. N. Sharpley, et al. (2001). "Processes controlling soil phosphorus release to runoff and implications for agricultural management." Nutrient Cycling in Agroecosystems 59(3): 269-284.

McDowell, R. W. and I. Stewart (2005). "An improved technique for the determination of organic phosphorus in sediments and soils by31P nuclear magnetic resonance spectroscopy." Chemistry and Ecology 21(1): 11-22.

McDowell, R. W., T. J. van der Weerden, et al. (2011). "Nutrient losses associated with irrigation, intensification and management of land use: A study of large scale irrigation in North Otago, New Zealand." Agricultural Water Management 98(5): 877-885.

McLaughlin, M. J., T. M. McBeath, et al. (2011). "The chemical nature of P accumulation in agricultural soils—implications for fertiliser management and design: an Australian perspective." Plant and Soil 349(1-2): 69-87.

Monaghan, R. M., C. A. M. de Klein, et al. (2008). "Prioritisation of farm scale remediation efforts for reducing losses of nutrients and faecal indicator organisms to waterways: A case study of New Zealand dairy farming." Journal of Environmental Management 87(4): 609-622.

Negassa, W. and P. Leinweber (2009). "How does the hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: a review." Journal of Plant Nutrition and Soil Science 172(3): 305-325.

Nziguheba, G., C. A. Palm, et al. (1998). "Soil phosphorus fractions and adsorption as affected by organic and inorganic sources." Plant and Soil 198(2): 159-168.

O'Connor, M. B., R. D. Longhurst, et al. (2001). "Fertilizer requirements for peat soils in the Waikato region." Proceedings of the New Zealand Grassland Association 63: 47-51.

Olsen, S.R., Cole, C.V., Watanabe, F.S. & Dean, L.A. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. USDA, Washington DC.

Pote, D.H. & Daniel, T.C. 2009. Dissolved phosphorus in water samples. In: Kovar & Pierzynski (Eds). Methods for phosphorus analysis. Southern Cooperative Series Bulletin 408. USDA.

Ron Vaz, M. D., A. C. Edwards, et al. (1993). "Phosphorus Fractions in Soil Solution: Influence of Soil Acidity and Fertiliser Additions." Plant and Soil 148: 175-183.

Rowland, A.P. & Haygarth, P.M. 1997. Determination of total dissolved phosphorus in soil solutions. Journal of Environmental Quality. 26: 410-415.

Saunders, W. M. H. (1965). "Phosphate retention by New Zealand soils and its relationship to free sequioxides, organic matter and other properties." New Zealand Journal of Agricultural Research 8: 30-57.

Sharpley, A. N., S. J. Smith, et al. (1992). "The Transport of Bioavailable Phosphorus in Agricultural Runoff." Journal of Environmental Quality 21: 30-35.

Sturman, A. and N. Tapper (2006). "The weather and climate of Australia and New Zealand."

Toor, G. S., L. M. Condron, et al. (2005). "Preferential phosphorus leaching from an irrigated grassland soil." European Journal of Soil Science 56(2): 155-168.

Toor, G. S., L. M. Condron, et al. (2003). "Characterization of organic phosphorus in leachate from a grassland soil." Soil Biology and Biochemistry **35**(10): 1317-1323.

Turner, B. L., N. Mahieu, et al. (2003). "Phosphorus-31 nuclear magnetic resonance spectral assignments of phosphorus compounds in soil NaOH-EDTA extracts." Soil Science Society of America Journal 67(2): 497-510.

Valls-Cantenys, C., M. Iglesias, et al. (2012). "Speciation of phosphorus oxoacids in natural and waste water samples." Journal of Chromatography A 1231: 16-21.

Winder, M. (2012). "Limnology: Lake warming mimics fertilization." Nature Clim. Change 2(11): 771-772.

https://www.lawa.org.nz/explore-data/otago-region/river-quality/manuherikia-river/

Appendices

Appendix 1 Lysimeter chemistry results.

	Average of FRP (mg P/L)	Average of TFP (mg P/L)	Average of TP (mg P/L)
Control			
30/10/2015	0.088	0.150	0.234
4/11/2015	0.147	0.249	0.308
9/11/2015	0.144	0.321	0.343
13/11/2015	0.110	0.151	0.261
16/11/2015	0.029	0.187	0.261
23/11/2015	0.116	0.034	0.320
28/11/2015	0.128	0.160	0.243
4/12/2015	0.039	0.144	0.191
18/12/2015	0.072	0.185	0.249
11/01/2016	0.197	0.301	0.537
20/01/2016	0.294	0.468	0.600
16/03/2016	0.085	0.360	0.511
8/04/2016	0.046	0.051	0.491
Dung			
30/10/2015	0.161	0.120	0.364
4/11/2015	0.438	0.569	1.211
9/11/2015	0.224	0.934	0.855
13/11/2015	0.132	0.291	0.530
16/11/2015	0.096	0.376	0.523
23/11/2015	0.200	0.218	0.719
28/11/2015	0.156	0.349	0.483
4/12/2015	0.117	0.354	0.485
18/12/2015	0.306	0.575	1.397
11/01/2016	0.015	0.112	1.362
20/01/2016	0.748	0.948	1.192
16/03/2016	0.239	0.261	0.960
8/04/2016	0.099	0.155	0.765

*Treatments applied 28/10/2015.

Average of FRP (mg P/L)		Average of TFP (mg P/L)	Average of TP (mg P/L)
Super 50kg P/ha			
30/10/2015	0.067	0.182	0.276
4/11/2015	0.603	2.760	3.547
9/11/2015	0.673	1.211	1.073
13/11/2015	0.425	0.468	0.610
16/11/2015	0.317	0.434	0.493
23/11/2015	0.276	0.184	0.448
28/11/2015	0.237	0.301	0.400
4/12/2015	0.164	0.312	0.318
18/12/2015	0.108	0.221	0.336
11/01/2016	0.472	0.686	0.898
20/01/2016	0.597	0.592	0.852
16/03/2016	0.136	0.178	0.628
8/04/2016	0.129	0.119	0.547
Super+dung 100 kg/ha			
30/10/2015	0.051	0.119	0.277
4/11/2015	0.450	1.592	2.511
9/11/2015	0.430	1.337	1.273
13/11/2015	0.230	0.469	0.711
16/11/2015	0.141	0.482	0.616
23/11/2015	0.215	0.222	0.882
28/11/2015	0.290	0.451	0.669
4/12/2015	0.381	0.771	0.699
18/12/2015	0.367	0.609	0.806
11/01/2016	0.130	0.187	1.352
20/01/2016	0.738	0.876	1.173
16/03/2016	0.155	0.245	0.825
8/04/2016	0.141	0.198	0.619

	Average PP (mg/L)	Average FURP (mg/L)		Average PP (mg/L)	Average FURP (mg/L)
Control			**Super 50kg P/ha**		
30/10/2015	0.084	0.061	30/10/2015	0.094	0.116
4/11/2015	0.059	0.102	4/11/2015	0.787	2.156
9/11/2015	0.023	0.177	9/11/2015	-0.138	0.537
13/11/2015	0.110	0.041	13/11/2015	0.143	0.043
16/11/2015	0.074	0.158	16/11/2015	0.059	0.117
23/11/2015	0.286	-0.082	23/11/2015	0.264	-0.091
28/11/2015	0.083	0.032	28/11/2015	0.099	0.065
4/12/2015	0.047	0.105	4/12/2015	0.006	0.148
18/12/2015	0.064	0.113	18/12/2015	0.116	0.113
11/01/2016	0.236	0.104	11/01/2016	0.027	0.179
20/01/2016	0.132	0.174	20/01/2016	0.259	-0.005
16/03/2016	0.065	0.290	16/03/2016	0.450	0.042
8/04/2016	0.358	0.005	8/04/2016	0.428	-0.010
Dung			**Super+dung 100 kg P/ha**		
30/10/2015	0.243	-0.041	30/10/2015	0.158	0.068
4/11/2015	0.642	0.131	4/11/2015	0.919	1.142
9/11/2015	-0.079	0.710	9/11/2015	-0.064	0.907
13/11/2015	0.239	0.160	13/11/2015	0.242	0.239
16/11/2015	0.147	0.280	16/11/2015	0.134	0.341
23/11/2015	0.501	0.018	23/11/2015	0.660	0.006
28/11/2015	0.134	0.193	28/11/2015	0.217	0.161
4/12/2015	0.131	0.236	4/12/2015	-0.072	0.390
18/12/2015	0.822	0.269	18/12/2015	0.197	0.242
11/01/2016	1.249	0.098	11/01/2016	0.971	0.047
20/01/2016	0.244	0.200	20/01/2016	0.297	0.138
16/03/2016	0.698	0.022	16/03/2016	0.580	0.090
8/04/2016	0.610	0.057	8/04/2016	0.421	0.057

	Average of TP Load (mg/kg)		
Control		**Super 50kg P/ha**	
30/10/2015	233.96	30/10/2015	276.40
4/11/2015	135.40	4/11/2015	1837.10
9/11/2015	343.27	9/11/2015	1072.58
13/11/2015	260.80	13/11/2015	610.42
16/11/2015	260.84	16/11/2015	493.44
23/11/2015	319.68	23/11/2015	448.00
28/11/2015	242.84	28/11/2015	400.41
4/12/2015	190.88	4/12/2015	318.41
18/12/2015	249.35	18/12/2015	336.26
11/01/2016	536.67	11/01/2016	598.80
20/01/2016	600.18	20/01/2016	851.64
16/03/2016	247.38	16/03/2016	520.30
8/04/2016	409.12	8/04/2016	546.50
Dung		**Super+dung 100 kg P/ha**	
30/10/2015	363.93	30/10/2015	276.93
4/11/2015	996.44	4/11/2015	1796.92
9/11/2015	803.69	9/11/2015	1272.84
13/11/2015	530.15	13/11/2015	711.26
16/11/2015	522.71	16/11/2015	615.91
23/11/2015	719.13	23/11/2015	881.52
28/11/2015	483.00	28/11/2015	668.57
4/12/2015	484.67	4/12/2015	699.26
18/12/2015	1396.91	18/12/2015	805.78
11/01/2016	1330.59	11/01/2016	339.01
20/01/2016	1191.93	20/01/2016	1172.91
16/03/2016	753.54	16/03/2016	825.01
8/04/2016	765.23	8/04/2016	618.68

Appendix 2 Otago Regional Council results for Lysimeter site.

Irrigation water results for ORC site.

	Irrigation water				
Date	TP (mg P/L)	FRP (mg P/L)	Date	TP (mg P/L)	FRP (mg P/L)
12/09/2011	0.3	0.139	10/10/2012	0.59	0.23
11/10/2011	4.1	2.8	8/11/2012	1.33	0.73
19/10/2011	0.156	0.007	22/11/2012	2.5	1.74
31/10/2011	0.77	0.146	13/12/2012	0.71	0.34
4/11/2011	0.32	0.017	3/01/2013	0.77	0.48
22/11/2011	1.94	0.87	15/01/2013	0.085	0.006
5/12/2011	1.81	0.77	30/01/2013	1.01	0.41
20/12/2011	8.4	3.7	11/02/2013	0.22	0.005
5/01/2012	1.31	0.38	25/02/2013	1.67	0.48
17/01/2012	2	0.56	18/03/2013	4.4	2.5
1/02/2012	0.33	0.062	7/05/2013	1.39	0.26
7/02/2012	0.088	0.014	29/05/2013	3.2	1.47
15/02/2012	0.033	0.014	5/06/2013	2.3	1.49
22/02/2012	0.61	0.56	26/06/2013	1.19	0.67
24/02/2012	0.08	0.063	16/09/2013	0.68	0.006
15/03/2012	3.5	2.2	4/10/2013	0.89	0.026
28/03/2012	1.25	0.002	23/10/2013	0.21	0.002
19/04/2012	10.6	4.4	6/11/2013	0.66	0.014
7/05/2012	1	0.33	21/11/2013	3.6	1.08
22/05/2012	0.75	0.085	10/12/2013	1.11	0.115
29/05/2012	23	10	23/12/2013	0.31	0.004
25/06/2012	0.52	0.35	7/01/2014	1.92	0.26
24/07/2012	0.22	0.039	22/01/2014	1.62	0.36
10/09/2012	0.064	0.008	3/02/2014	8.1	1.39

*** Where no results for a given date was recorded, that date has been omitted.**

Lysimeter - East arm results for ORC site.

	Lysimeter - East arm		
Date	TP (mg P/L)	FRP (mg P/L)	Volume (L)
22/11/2011	0.196	0.040	24.25
5/12/2011	0.077	0.015	0.35
20/12/2011	0.27	0.093	1.8
5/01/2012	0.098	0.016	0.2
17/01/2012	0.18	0.006	7.62
1/02/2012	0.139	0.023	6.45
15/02/2012	0.46	0.184	32
22/02/2012	2.9	2.700	32.2
24/02/2012	0.87	0.620	32
15/03/2012	0.4	0.260	15.5
19/04/2012	0.39	0.290	4.62
7/05/2012	0.36	0.280	2.74
29/05/2012	0.46	0.240	0.51
8/11/2012	0.28	0.187	15.35
22/11/2012	0.25	0.102	10.74
13/12/2012	0.51	0.330	12.25
3/01/2013	0.31	0.230	11.5
15/01/2013	0.26	0.124	9.43
30/01/2013	0.65	0.260	6.74
11/02/2013	0.31	0.210	5.57
18/03/2013	0.32	0.270	0.95
7/05/2013	0.27	0.200	3.39
29/05/2013	0.155	0.136	3.06
5/06/2013	0.175	0.114	19.5
26/06/2013	0.123	0.094	23.6
16/09/2013	0.088	0.080	0.4
4/10/2013	0.25	0.176	16.5
23/10/2013	0.21	0.185	0.93
6/11/2013	0.24	0.184	1.58
21/11/2013	0.66	0.420	31.9
10/12/2013	0.51	0.410	
23/12/2013	0.38	0.170	21.59
7/01/2014	0.39	0.330	25.5
22/01/2014	0.29	0.270	3.04
3/02/2014	0.34	0.290	6.75

*** Where no results for a given date was recorded, that date has been omitted.**

Lysimeter - South arm results for ORC site.

Date	Lysimeter - South arm		
	TP (mg P/L)	FRP (mg P/L)	Volume (L)
20/12/2011	0.42	0.004	7.05
5/01/2012	0.44	0.062	29
17/01/2012	0.54	0.220	17.77
1/02/2012	0.55	0.007	30.6
7/02/2012	0.56	0.250	0.13
15/02/2012	0.46	0.250	31.6
22/02/2012	0.86	0.780	24.42
24/02/2012	0.91	0.290	27
15/03/2012	0.27	0.220	10.7
28/03/2012	0.25	0.157	3.66
7/05/2012	0.193	0.145	4.23
22/05/2012	0.187	0.144	0.66
10/09/2012	0.166	0.130	1.7
10/10/2012	0.2	0.178	0.82
7/05/2013	0.08	0.002	0.3
5/06/2013	0.079	0.046	11.2
26/06/2013	0.074	0.062	18.5
16/09/2013	0.114	0.066	0.2
23/10/2013	0.081	0.039	1.86
21/11/2013	0.77	0.550	32
10/12/2013	0.54	0.400	
23/12/2013	1.76	0.057	31.43
7/01/2014	2.2	1.670	31.52
22/01/2014	3	2.400	32
3/02/2014	2.6	2.300	32

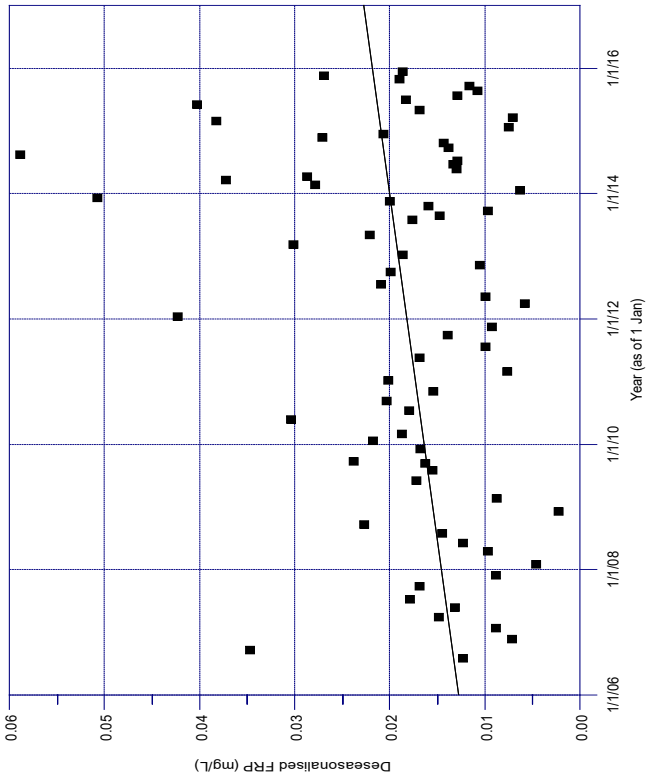
*** Where no results for a given date was recorded, that date has been omitted**

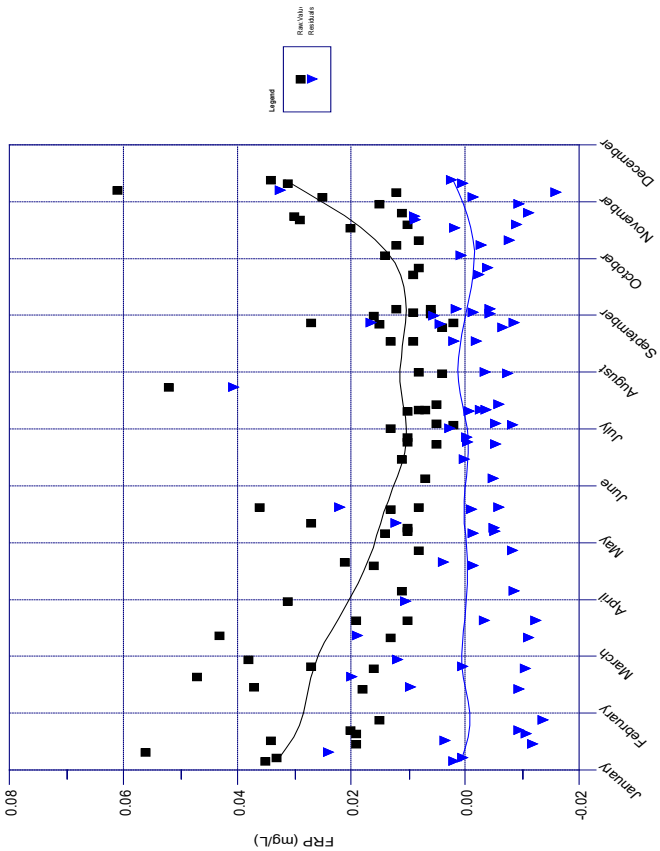
Trial observations and activities for ORC site.

Date	Comments
5/12/2011	2-3 December 300 cows grazed paddock
20/12/2011	Pivot irrigation applied effluent 7/12/11
15/02/2012	8-9 Feb cows grazed paddock
22/02/2012	450 kg SP applied 16/02/12
15/03/2012	Pivot irrigation applied effluent 5-6th March, Cows grazed 13 - 14 March
19/04/2012	Pivot irrigation applied effluent 30-31 March and 12 -13 April
7/05/2012	Cows grazed paddock 21-23 April
29/05/2012	Pivot irrigatior applied effluent 25/05/12
10/09/2012	Cows grazed paddock 12-15 August
8/11/2012	Cows grazed paddock 11-13 October and 5 - 7 Nov. Pivot irrigation of effluent 25-26 October
22/11/2012	Pivot irrigation applied effluent 15 Nov and 5 Dec. Paddock cut for silage 10 Dec.
15/01/2013	Cows grazed paddock 4-6 Jan. Pivot irrigation of effluent 8th Jan
30/01/2013	Piovt irrigation of effluent 29 Jan
25/02/2013	Cows grazed paddock 12-14 Feb. 400 kg Super P applied 15 Jan.
18/03/2013	Pivot irrigation applied effluent 1 March. Cows grazed paddock 10-12 March
7/05/2013	Pivot irrigation applied effluent 8 April. Cows grazed paddock 6 - 8 April and 3-5 May
26/06/2013	Pivot irrigation applied effluent 21 June

Appendix 3 Manuherikia River FRP trend analysis 2010-2016.

DeSeasonalised trend analysis of 2010-2016 FRP data obtained from Land, Air and Water Aotearoa (LAWA).





Equivalence test of deseasonalised slope

Significance level is 0.050000000000

The slope of the trend line fitted to deseasonalised data is 0.000002486550 (0.000908211000 per year or 4.995510000000% per year)